P.B.5818 – Patentlaan 2
2280 HV Rijswijk (ZH)
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Lane, Cathal Michael
c/o Tomkins & Co.
5 Dartmouth Road
Dublin 6
IRLANDE

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22.07.02

Zeichen/Ref./Réf.	Anmeldung Nr./Application No./Demande n°./Patent Nr./Patent No./Brevet n°.
PN029EP	00942630.5-2102-US0011878

Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire
LOCTITE CORPORATION

COMMUNICATION

The European Patent Office herewith transmits as an enclosure the European search report for the above-mentioned European patent application.

If applicable, copies of the documents cited in the European search report are attached.

[X] Additional set(s) of copies of the documents cited in the European search report is (are) enclosed as well.

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REFUND OF THE SEARCH FEE

If applicable under Article 10 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.

European Patent Office

SUPPLEMENTARY EUROPEAN SEARCH REPORT

Application Number
EP 00 94 2630

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 04, 31 March 1998 (1998-03-31) -& JP 09 316421 A (SUMITOMO SEIKA CHEM CO LTD), 9 December 1997 (1997-12-09) * abstract *	1,4,5,8, 9	H01L21/56 H01L21/58 C08K3/36 C08L63/00 C08L69/00 C08L71/00
X	CHEMICAL ABSTRACTS, vol. 100, no. 20, 14 May 1984 (1984-05-14) Columbus, Ohio, US; abstract no. 157412, SERGEEV ET AL.: "Diglycidyl aromatic thio ethers and epoxy polymers derived from them" XP002932993 * abstract *	1,4,5,8	
X	& VYSOKOMOL. SOEDIN., SER.A(1984), 26(1),208-211,	1,4,5,8	
X	US 5 512 613 A (AFZALI-ARDAKANI ALI ET AL) 30 April 1996 (1996-04-30) * column 6, line 21-60 * * column 7, line 10 - column 8, line 12 *	1-4,9, 13,14, 17,18, 25-30	TECHNICAL FIELDS SEARCHED (Int.Cl.7) H01L C08L C08K C08G
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 443 (C-1239), 18 August 1994 (1994-08-18) -& JP 06 136092 A (NEW JAPAN CHEM CO LTD), 17 May 1994 (1994-05-17) * abstract *	1,2,4,9, 10,13, 14,26	

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The supplementary search report has been based on the last set of claims valid and available at the start of the search.

Place of search	Date of completion of the search	Examiner
MUNICH	11 July 2002	Marquis, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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EPO FORM 1503 03.82 (P04C04)

European Patent Office

SUPPLEMENTARY EUROPEAN SEARCH REPORT

Application Number
EP 00 94 2630

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 05, 31 May 1996 (1996-05-31) -& JP 08 012741 A (NEW JAPAN CHEM CO LTD), 16 January 1996 (1996-01-16) * abstract *	1,2,4,9, 10,26	
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X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 433 (C-543), 15 November 1988 (1988-11-15) -& JP 63 159426 A (SUMITOMO BAKELITE CO LTD), 2 July 1988 (1988-07-02) * abstract *	1,2,9, 13,14,17	
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 528 (C-1258), 6 October 1994 (1994-10-06) -& JP 06 184409 A (TOKUYAMA SODA CO LTD), 5 July 1994 (1994-07-05) * abstract *	1,3, 11-13, 17,18	TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The supplementary search report has been based on the last set of claims valid and available at the start of the search.

Place of search	Date of completion of the search	Examiner
MUNICH	11 July 2002	Marquis, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 94 2630

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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11-07-2002

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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PA..NT COOPERATION TREAT

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

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in its capacity as elected Office.

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International filing date (day/month/year) 16 June 2000 (16.06.00)	**Priority date** (day/month/year) 17 June 1999 (17.06.99)
Applicant DOBA, Takahisa	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

08 December 2000 (08.12.00)

[ ] in a notice effecting later election filed with the International Bureau on:

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(71) Applicants *(for all designated States except US)*: **LOCTITE CORPORATION** [US/US]; Legal Dept., 1001 Trout Brook Crossing, Rocky Hill, CT 06067 (US). **LOCTITE (JAPAN) CORPORATION** [JP/JP]; 15-13, Fukuura 1-chome, Kanazawa-ku, Yokohama 236 (JP).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **DOBA, Takahisa** [JP/JP]; 3-18-7, Noukendai, Kanazawa-ku, Yokohama 236-0057 (JP).

(74) Agent: **BAUMAN, Steven, C.**; Loctite Corporation, 1001 Trout Brook Crossing, Rocky Hill, CT 06067 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

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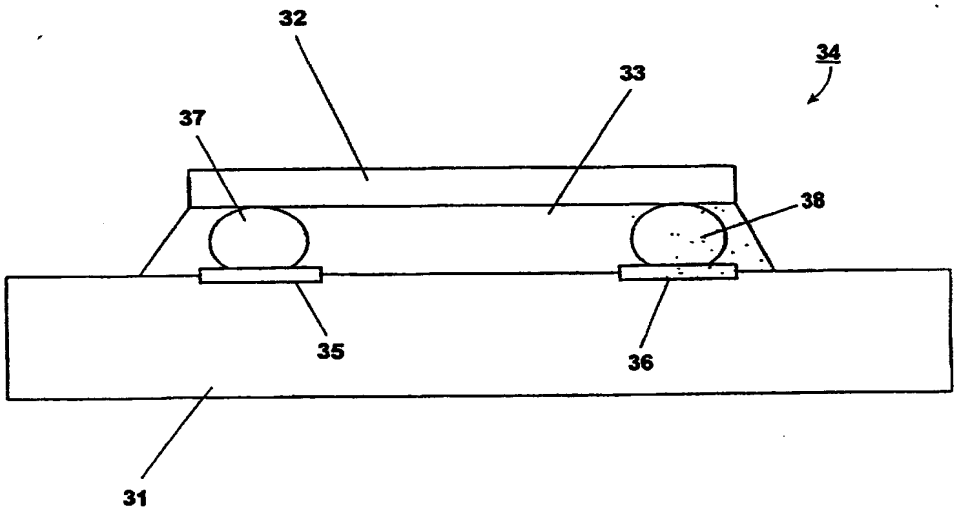
[Continued on next page]

(54) Title: CONTROLLABLY DEGRADABLE COMPOSITION OF HETEROATOM CARBOCYCLIC OR EPOXY RESIN AND CURING AGENT



(57) Abstract: A reworkable underfilling sealing mateiral (33) for the attachment of a semiconductor device (32) to a carrier substrate (31) is prepared from a composition comprising a curable resin (a) which is a resin with a (thio)ether or carbonate core structure and a heteroatom-containing carbocyclic structure, an epoxy resin having at least one alkylene oxide residue, or an epoxy resin with a monepoxide (thio)ester or carbonate coreactant diluent; and (b) a curing agent including a polyamine, an epoxy- or novolac-modified amine, an amide compound or an imidazole; optionally with an anhydride.

WO 00/79582 A1

— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

CONTROLLABLY DEGRADABLE COMPOSITION OF HETEROATOM CARBOCYCLIC OR EPOXY RESIN AND CURING AGENT

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to thermosetting resin compositions useful for mounting onto a circuit board semiconductor devices, such as chip size or chip scale packages ("CSPs"), ball grid arrays ("BGAs"), land grid arrays ("LGAs") and the like, each of which having a semiconductor chip, such as large scale integration ("LSI"), on a carrier substrate. Similarly, the compositions are useful for mounting onto circuit board semiconductor chips themselves. Reaction products of the compositions of this invention are controllably reworkable when subjected to appropriate conditions.

Brief Description of Related Technology

In recent years, the popularity of small-sized electronic appliances, such as camera-integrated video tape

recorders ("VTRs") and portable telephone sets, has made size reduction of LSI devices desirable. As a result of these reduction desires, CSPs, BGAs and LGAs are being used to reduce the size of packages substantially to that of bare chips. Such CSPs, BGAs and LGAs improve the characteristics of the electronic device while retaining many of their operating features, thus serving to protect semiconductor bare chips, such as LSIs, and facilitate testing thereof.

Ordinarily, the CSP/BGA/LGA assembly is connected to electrical conductors on a circuit board by use of a solder connection or the like. However, when the resulting CSP/BGA/LGA/circuit board structure is exposed to thermal cycling, vibration, distortion or is dropped, the reliability of the solder connection between the circuit board and the CSP/BGA/LGA often becomes suspect. Recently, after a CSP/BGA/LGA assembly is mounted on a circuit board, the space between the CSP/BGA/LGA assembly and the circuit board is often now filled with a sealing resin (commonly referred to as underfill sealing) in order to relieve stresses caused by thermal cycling, thereby improving heat shock properties and enhancing the reliability of the structure.

However, since thermosetting resins that form cross linked networks when cured are typically used as the underfill sealing material, in the event of a failure after the CSP/BGA/LGA assembly is mounted on the circuit board, it is difficult to replace the CSP/BGA/LGA assembly without destroying or scrapping the CSP/BGA/LGA assembly-circuit board structure in its entirety.

To that end, techniques for mounting a semiconductor chip on a circuit board are accepted as substantially similar to the mounting of a CSP/BGA/LGA assembly onto a circuit board. One such technique, disclosed in Japanese Laid-Open

Patent Publication No. 102343/93, involves a mounting process where a semiconductor chip is fixed and connected to a circuit board by use of a photocurable adhesive. In the event of failure, this semiconductor chip is removable. However, this technique requires the circuit board to be a transparent substrate (e.g., glass) which permits exposure to light from the back side. Since the circuit board is constructed of such a substrate, the resulting structure often exhibits poor heat shock resistance.

Japanese Laid-Open Patent Publication No. 69280/94 discloses a process where a semiconductor chip is fixed and connected to a substrate by use of a resin capable of hardening at a predetermined temperature. In the event of failure, the semiconductor chip is removed from the substrate by softening the resin at a temperature higher than the predetermined temperature. No specific resin is disclosed, and there is no discussion regarding treating the resin that remains on the substrate. Thus, the disclosed process is at best incomplete.

As pointed out in U.S. Patent No. 5,423,931 (Inoue), it is conventional to use a solvent to remove residual resin from a circuit board. However, swelling the resin with a solvent is a time-consuming process and the corrosive organic acid ordinarily used as the solvent may reduce the reliability of the circuit board. Instead, the '931 patent speaks to a method for removing residual resin by irradiation with electromagnetic radiation.

Japanese Laid-Open Patent Publication No. 251516/93 also discloses a mounting process using a bisphenol A type epoxy resin (CV5183 or CV5183S; manufactured by Matsushita Electric Industrial Co., Ltd.). However, the removal process disclosed does not consistently permit easy removal of the

chip, the curing step is lengthy at elevated temperatures, and the process generally results in poor productivity.

Of course, mechanical methods of removing/replacing semiconductor chips from/on a substrate are known, such as by cutting the chip to be removed/replaced. See U.S. Patent No. 5,355,580 (Tsukada).

Thermoplastic underfill resins are known for use in semiconductor chip attachment. See U.S. Patent No. 5,783,867 (Belke, Jr.). However, such thermoplastic resins tend to leak under relatively modest temperature conditions. In contrast, thermosetting resins cure into a matrix, which ordinarily have greater thermal stability under end use operating temperatures.

U.S. Patent Nos. 5,512,613 (Afzali-Ardakani), 5,560,934 (Afzali-Ardakani), and 5,932,682 (Buchwalter), each refer to a reworkable thermoset composition based on a diepoxide component in which the organic linking moiety connecting the two epoxy groups of the diepoxide includes an acid cleavable acyclic acetyl group. With such acid cleavable acyclic acetyl groups forming the bases of the reworkable composition, a cured thermoset need only be introduced to an acidic environment in order to achieve softening and a loss of much of its adhesiveness.

U.S. Patent No. 5,872,158 (Kuczynski) refers to thermosetting compositions capable of curing upon exposure to actinic radiation, which are based on acetyl diacrylates, and reaction products of which are reported to be soluble in dilute acid.

U.S. Patent No. 5,760,337 (Iyer) refers to thermally reworkable crosslinked resins to fill the gap created between a semiconductor device and a substrate to which it is attached. These resins are produced by reacting a dienophile

(with a functionality greater than 1) with a 2.5-dialkyl substituted furan-containing polymer.

International Patent Publication No. PCT/US98/00858 refers to a thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected. The composition includes about 100 parts by weight of an epoxy resin, about 3 to about 60 parts by weight of a curing agent, and about 1 to about 90 parts by weight of a plasticizer. There, the area around the cured thermoset is heated at a temperature of about 190 to about 260^{0}C for a period of time ranging from about 10 seconds to about 1 minute in order to achieve softening and a loss of much of its adhesiveness.

U.S. Patent Nos. 5,948,922 (Ober) and 5,973,033 (Ober), each refer to a certain class of compounds having tertiary oxycarbonyl linkages, and compositions based on such compounds, which when cured provide thermally decomposable compositions capable of being reworked.

Notwithstanding the state-of-the-art, it would be desirable for an underfilling sealing material to provide good productivity and thermal shock resistance, while allowing the substrates with which it is to be used to be readily processed and easily separated from a semiconductor device without too extreme conditions that may compromise the integrity of the semiconductor devices remaining on the substrate or the substrate itself.

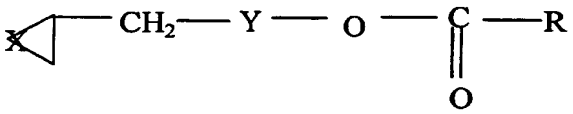
SUMMARY OF THE INVENTION

The present invention provides a thermosetting resin composition useful as an underfill sealant resin. The

composition enables a semiconductor device, such as a CSP/BGA/LGA assembly which includes a semiconductor chip mounted on a carrier substrate, to be securely connected to a circuit board by short-time heat curing and with good productivity, which demonstrates excellent heat shock properties (or thermal cycle properties), and permits the CSP/BGA/LGA assembly to be easily removed from the circuit board in the event of semiconductor device or connection failure. Similarly, a semiconductor chip may be securely connected to, and if necessary removed from, a circuit board using the inventive compositions.

The thermosetting resin composition includes a curable resin component and a curing agent. The curable resin component may be chosen from those having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one linkage selected from ether, thioether, carbonate and combinations thereof, which linkage is capable of being reworked under appropriate conditions so as to lose its adhesiveness. One such rework technique involves degrading the cured reaction product of the composition upon exposure to elevated temperature conditions and/or acidic conditions. In addition, the curable resin may be an epoxy resin, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group. Where the curable resin is not an epoxy resin, the inventive composition may include as a separate component an epoxy resin component.

The compositions may also include a monofunctional epoxy coreactant diluent represented by the following structure:



where X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents alkyl, alkenyl, aryl and the like; and R represents alkyl, alkenyl, aryl and the like, as well as an inorganic filler component. In addition, where the curing agent is not an anhydride, the inventive compositions may also include a separate anhydride component.

Reaction products of these compositions are capable of being controllably reworked through the softening and loss of their adhesiveness, such as by exposure to temperature conditions in excess of those used to cure the composition.

Although the thermosetting resin composition of the present invention is curable at a relatively low temperature in a short period of time, cured reaction products thereof have excellent heat shock properties and, moreover, can be easily split by the application of force under heated conditions. That is, semiconductor devices or semiconductor chips attached to circuit boards by cured reaction products of the thermosetting resin compositions of this invention can be easily removed by heating the reaction product, allowing it to swell with a solvent, or allowing it to swell with a solvent under heated conditions.

By using the thermosetting resin compositions of this invention, semiconductor devices, such as CSP/BGA/LGA assemblies, or semiconductor chips can be securely connected to a circuit board by short-time heat curing and with good productivity, with the resulting mounting structure demonstrating excellent heat shock properties (or thermal cycle properties). Moreover, in the event of failure, the

semiconductor device or semiconductor chip can be easily removed. This makes it possible to reuse the circuit board, thereby achieve an improvement in the yield of the production process and reducing production cost.

The benefits and advantages of the present invention will become more readily apparent after a reading the "Detailed Description of the Invention", with reference to the figures.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 depicts a cross-sectional view showing an example of a semiconductor device in which the thermosetting resin composition of the present invention is used.

FIG. 2 depicts a cross-sectional view of a semiconductor device which has been removed from the circuit board for repairing purposes.

FIG. 3 depicts a cross-sectional view showing an example of a semiconductor flip chip assembly in which the thermosetting resin composition of the present invention is used.

FIG. 4 depicts a flow diagram of a procedure useful to rework a cured thermosetting resin composition in accordance with the present invention, so as to remove a semiconductor device from a circuit board to which it had been attached.

FIG. 5 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (■) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin ( ) loses weight by virtue of thermal degradation.

FIG. 6 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (■) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin (□) loses weight by virtue of thermal degradation.

FIG. 7 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (◆) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin (◇) loses weight by virtue of thermal degradation.

FIG. 8 depicts a ^{13}C NMR spectra of "ANCAMINE" 2337S.

FIG. 9 depicts a FT-IR spectra of "ANCAMINE" 2337S.

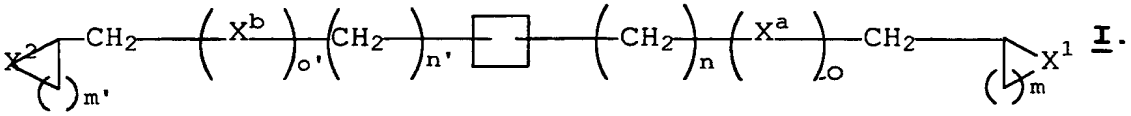
DETAILED DESCRIPTION OF THE INVENTION

The thermosetting resin composition broadly includes a curable resin component and a curing agent.

The curable resin component may be chosen from those having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one linkage selected from ether, thioether, carbonate and combinations thereof, which linkage is capable of being reworked under appropriate conditions so as to lose its adhesiveness. One such rework technique involves degrading the cured reaction product of the inventive composition upon exposure to elevated temperature conditions and/or acidic conditions. In addition, the curable resin may be an epoxy resin, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one

terminal epoxy group. Where the curable resin is not itself an epoxy resin, the inventive composition may include as a separate component an epoxy resin component.

In one aspect of the invention, the curable resin may be represented by the following structure:

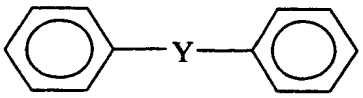


I.

The box may represent one or more structural linkages including aromatic rings(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms, examples of which are given below.

X^1, X^2 and X^a and X^b may be the same or different and represent the heteroatoms, oxygen and sulfur. The letter designations, m and m^1, represent integers within the range of 1 to 3, n and n^1 represent integers within the range of 0 to 8, and o and o^1 represent integers within the range of 1 to 3. The box of the core structure of aromatic rings within the curable resin of structure I may be individual aromatic rings, or aromatic ring systems having multiple aromatic units joined in fused ring systems, joined in bi-aryl (such as, biphenyl) or bis-aryl (such as bisphenol A or bisphenol F, or bisphenol compounds joined by a heteroatom) systems, joined in cycloaliphatic-aromatic hybrid ring systems, or joined in oligomeric (such as, novolac-type) systems, examples of which include, among others, naphthalene, anthracene, phenanthracene and fluorene.

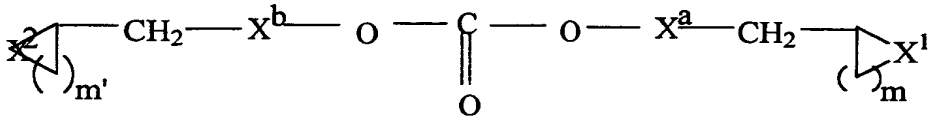
For instance, the box may represent the structural linkage



where Y may or may not be present and when present is carbon, or the heteroatom, oxygen or sulfur. Or the box may represent a phenylene group. Either of these representations may bear substitution at one or more locations on the aromatic ring(s) with functional groups ordinarily present on aromatic rings(s), such as alkyl, alkenyl, halo, nitro, carboxyl, amino, hydroxyl, thio, and the like.

For instance, particularly desirable curable resins within structure I include MPG, [bis[4(2,3-epoxy-propylthio)phenyl]-sulfide (CAS Reg. No. 84697-35-8), available commercially from Sumitomo Seika Chemicals Co., Ltd., Osaka, Japan and XBO, xylene bisoxetane (CAS Reg. No. 142627-97-2), available commercially from UBE Industries, Ltd., Tokyo, Japan.

In another aspect of the invention, the curable resin is represented by the following structure:



II.

X^1 and X^2 are as above; X^a and X^b may be the same or different, may or may not be present, and when present represent alkyl, alkenyl, aryl and the like; and the letter designations, m and m^1 are as above.

The heteroatom-containing carbocyclic structures pending from the core structure may be three, four or five membered rings with the heteroatom being an oxygen and/or sulfur atom. These ring structures cross-link with one another under appropriate conditions to form reaction products of the compositions of the present invention.

The carbonate linkage is degradable upon exposure to elevated temperature conditions, with or without the presence of acid. This linkage is capable of degrading to liberate carbon dioxide gas.

The temperature used to effect such degradation of compositions within the scope of the present invention may be as great as 50°C lower than the temperatures required to degrade ordinary epoxy-based compositions used for this purpose, such as those based on bisphenol-A-type epoxy resins or bisphenol-F-type epoxy resins, which are ordinarily in the vicinity of about 300°C or more. (See Examples section.)

A particularly desirable curable resin within structure II includes CBO, carbonate bisoxetane (CAS Reg. No. 60763-95-3), available commercially from UBE Industries, Ltd., Tokyo, Japan.

In still another aspect of the invention, the curable resin is an epoxy resin, where at least a portion of such epoxy resin includes an epoxy resin having at least one alkylene oxide residue position adjacent at least one terminal epoxy group. The epoxy resin may be based on mono- or multi-functional aliphatic epoxies, epoxies with a cycloaliphatic ring structure or system, or epoxies with an aromatic ring structure or system, and combinations thereof

For instance the epoxy resin may include any common epoxy resin, such as a multifunctional epoxy resin.

Ordinarily, the multifunctional epoxy resin should be included in an amount within the range of about 15% by weight to about 75% by weight of the total of the epoxy resin component. In the case of bisphenol-F-type epoxy resin, desirably the amount thereof should be in the range of from about 35% by weight to about 65% by weight, such as about 40% by weight to about 50% by weight of the total of the epoxy resin component.

Examples of the multifunctional epoxy resin include bisphenol-A-type epoxy resin, bisphenol-F-type epoxy resin (such as RE-404-S from Nippon Kayaku, Japan), phenol novolac-type epoxy resin, and cresol novolac-type epoxy from resin (such as "ARALDITE" ECN 1871 from Ciba Specialty Chemicals, Hawthorne, New York).

Other suitable epoxy resins include polyepoxy compounds based on aromatic amines and epichlorohydrin, such as N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether; and N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate.

Among the epoxy resins suitable for use herein also include polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradename "EPON", such as "EPON" 828, "EPON" 1001, "EPON" 1009, and "EPON" 1031 from Shell Chemical Co.; "DER" 331, "DER" 332, "DER" 334, and "DER" 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of such as "DEN" 431, "DEN" 438, and "DEN" 439 from Dow Chemical. Cresol analogs are also available commercially under the tradename "ARALDITE", such as "ARALDITE" ECN 1235, "ARALDITE" ECN 1273, and "ARALDITE" ECN 1299 from Ciba Specialty Chemicals Corporation. SU-8 is a bisphenol-A-type epoxy

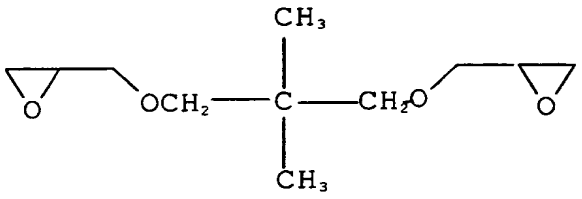
novolac available from Interez, Inc. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include GLYAMINE" 135, "GLYAMINE" 125, and "GLYAMINE" 115 from F.I.C. Corporation; "ARALDITE" MY-720, "ARALDITE" 0500, and "ARALDITE" 0510 from Ciba Specialty Chemicals and PGA-X and PGA-C from the Sherwin-Williams Co.

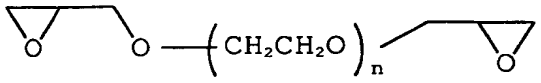
An of course combinations of the different epoxy resins are also desirable for use herein.

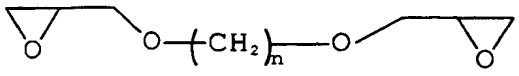
It is particularly desirable for the portion of the epoxy resin component having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group to be present in an amount of at least about 5% by weight of the total of epoxy resin component.

Examples of aliphatic epoxies with alkylene oxide residues include, but are not limited to, mono-, di- or multi-functional epoxies containing ether linkages, such as primary, secondary and tertary alkylene diol diglycidyl ethers, and epoxies containing mono- or poly-alkylene oxide residues (such as ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, and hexylene oxide residues).

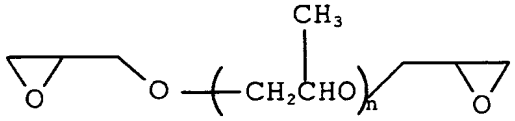
For instance,



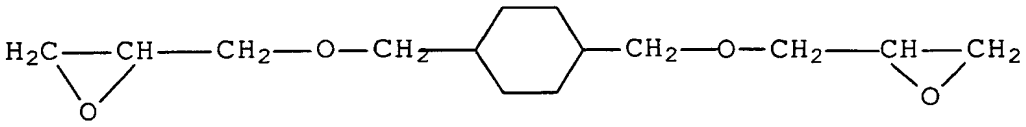




where n is an integer from 1 to about 18, are each appropriate, individually or in combination, for use as at least a portion of the epoxy resin component.

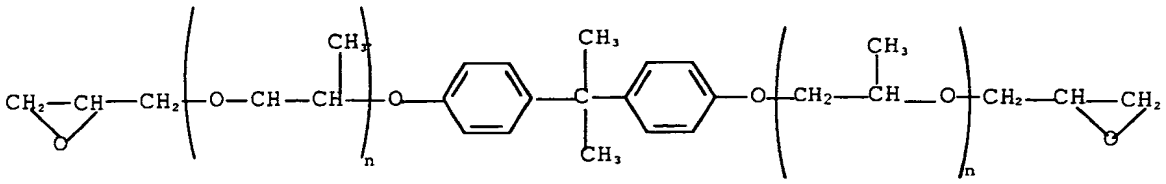


Examples of cycloaliphatic epoxies with alkylene oxide residues include mono-, di- or multi functional cyclohexyl epoxies; hydrated bisphenol A-type epoxies; and hydrated bisphenol F-type epoxies, containing alkylene ether residues. DME-100 (1,4-cyclohexane dimethanol diglycidyl ether, available commercially from New Japan Chemical Co., Ltd.) as shown below is one such example.

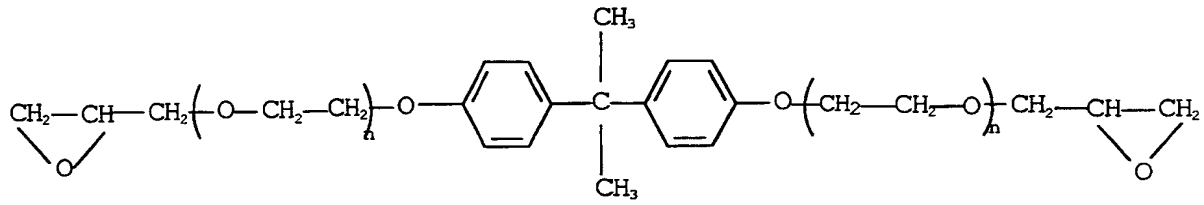


Examples of aromatic epoxies with alkylene oxide residues include mono-, di- or multi- functional epoxies such as bisphenol A type epoxies; bisphenol F type epoxies; phenol novolac type epoxies; and cresol novolac type epoxies, containing alkylene ether residues.

Examples of such epoxies include BEO-60E (ethoxylated bisphenol A di-glycidyl ether, available commercially from New Japan Chemical Co., Ltd.), and BPO-20E (propyloxylated bisphenol A di-glycidyl ether, available commercially from New Japan Chemical Co., Ltd.), which are shown below:



where n is an integer between and about 1 and 20, which for BPO-60E n is 1, and



where n is an integer between and about 1 and 20, which for BEO-60E n is 3.

The curable resin component should be present in the composition in an amount which the range of about 10% by weight to about 95% by weight, desirably about 20% by weight to about 80% by weight, such as about 60% by weight

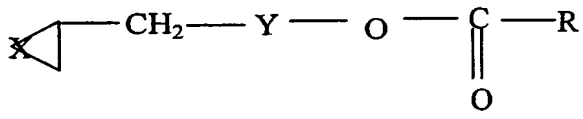
In yet another aspect of the invention, the epoxy resin is used in combination with a monofunctional epoxy coreactant diluent.

Appropriate monofunctional epoxy coreactant diluents for use herein include those that have a viscosity which is lower than that of the epoxy resin component, ordinarily, less than about 250 cps.

The monofunctional epoxy coreactant diluents should have an epoxy group with an alkyl group of about 6 to about 28 carbon atoms, examples of which include C_{6-28} alkyl glycidyl

ethers, C_{6-28} fatty acid glycidyl esters and C_{6-28} alkylphenol glycidyl ethers.

A particularly desirable coreactant diluent is represented by:



III.

where X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents an alkyl (linear, branched, cyclo or bicyclo), or alkenyl (linear, branched, cyclo or bicyclo) and the like linkage of from one to about twenty carbon atoms, linkage and an aryl (one or more aromatic ring(s) or ring system(s)) linkage of from about six to about twenty carbon atoms.

Commercially available monofunctional epoxy coreactant diluents include those from Pacific Epoxy Polymers, Richmond, Michigan, under the trade designations PEP-6770 (glycidyl ester of neodecandoic acid), PEP-6740 (phenyl glycidyl ether) and PEP-6741 (butyl glycidyl ether).

In the event such a monofunctional epoxy coreactant diluents is included, such coreactant diluent should be employed in an amount of up to about 5% by weight to about 15% by weight, such as about 8% by weight to about 12% by weight, based on the total weight of the composition.

As the curing agent, a variety of materials may be chosen including amine compounds, amide compounds, imidazole compounds, modified amine compounds and modified imidazole compounds (modified compound are also called derivatives thereof).

Examples of the amine compounds include aliphatic polyamines, such as diethylenetriamine, triethylenetetramine and diethylaminopropylamine; aromatic polyamines, such as m-

xylenediamine and diaminodiphenylamine; and alicyclic polyamines, such as isophoronediamine and menthenediamine.

Of course, combinations of these amine compounds are also desirable for use in the compositions of the present invention.

Examples of the amide compounds include cyano-functionalized amides, such as dicyandiamide.

Examples of the imidazole compounds include imidazole, isoimidazole, and substituted imidazoles -- such as alkyl-substituted imidazoles (e.g., 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole and addition products of an imidazole and trimellitic acid, 2-n-heptadecyl-4-methylimidazole and the like, generally where each alkyl substituent contains up to about 17 carbon atoms and desirably up to about 6 carbon atoms), and aryl-substituted imidazoles [e.g., phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, 2-(2-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-napthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-

methoxystyrylimidazole, and the like, generally where each aryl substituent contains up to about 10 carbon atoms and desirably up to about 8 carbon atoms].

Examples of commercial imidazole compounds are available from Air Products, Allentown, Pennsylvania under the trade designation "CUREZOL" 1B2MZ and from Synthron, Inc., Morganton, North Carolina under the trade designation "ACTIRON" NXJ-60.

Of course, combinations of these imidazole compounds are also desirable for use in the compositions of the present invention.

Examples of the modified amine compounds include epoxy amine additives formed by the addition of an amine compound to an epoxy compound, and examples of the modified imidazole compounds include imidazole adducts formed by the addition of an imidazole compound to an epoxy compound.

A commercially available modified amine compound particularly useful herein is "NOVACURE" HX-3722 (an imidazole/bisphenol A epoxy adduct dispersed in bisphenol A epoxy resin, commercially available from Asahi-Ciba Ltd.), and "MY-24" (an imidazole/bisphenol A epoxy adduct, commercially available from Ajinomoto Co., Ltd.).

Another such modified amine compound particularly useful herein is available commercially from Air Products and Chemicals, Inc., Allentown, Pennsylvania under the "ANCAMINE" 2337S tradename. "ANCAMINE" 2337S is described by Air Products as a modified aliphatic amine, which is a light yellow powder in appearance with a particle size of 90% $\leq$ 10 μ, whose melting point is in the range of 145-172^{0}F. "ANCAMINE" 2337S is reported to have an amine value of 260 (mg KOH/gram), and rapid reactivity above a temperature of 158^{0}F. It is believed that "ANCAMINE" 2337S is a novolac-type resin

that has been modified through reaction with aliphatic amines, such as polyamines, pyrazines, pyridines, pyroles and pyrazoles. (See FIGs. 8-9 for characterizing data.) The "ANCAMINE" 2337S itself is substantially insoluble at room temperature in conventional non-basic organic solvents, though was found to be soluble in pyridine.

The curing agent should be present in an amount with the range of about 5% by weight to about 90% by weight, desirably about 20% by weight to about 60% by weight, such as about 50% by weight of the total composition.

The compositions may also include an anhydride component where the curing agent of the compositions is not based on anhydride reactivity, as well as an inorganic filler component.

Appropriate anhydride compounds for use herein include mono- and poly-anhydrides, such as hexahydrophthalic anhydride ("HHPA") and methyl hexahydrophthalic anhydride ("MHHPA") (commercially available from Lindau Chemicals, Inc., Columbia, South Carolina, used individually or as a combination, which combination is available under the trade designation "LINDRIDE" 62C) and 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (commercially available from ChrisKev Co., Leewood, Kansas under the trade designation B-4400). In addition, "MTA-15" (mixture of glycol tris-anhydrotrimeritate and MHHPA, commercially available from New Japan Chemical Co., Ltd.) and "MH-700" (MHHPA, commercially available from New Japan Chemical Co., Ltd.) are particularly desirable choices.

Of course, combinations of these anhydride compounds are also desirable for use in the compositions of the present invention. When used, the anhydride compound may be present in an amount within the range of about 5% by weight to about

90% by weight, desirably about 10% by weight to about 60% by weight, such as about 40% by weight of the total composition.

As an inorganic filler component, many materials are potentially useful. For instance, the inorganic filler component may often include reinforcing silicas, such as fused silicas, and may be untreated or treated so as to alter the chemical nature of their surface. Virtually any reinforcing fused silica may be used.

Particularly desirable ones have a low ion concentration and are relatively small in particle size (e.g., in the range of about 2-10 microns, such as on the order of about 2 microns), such as the silica commercially available from Admatechs, Japan under the trade designation SO-E5.

Other desirable materials for use as the inorganic filler component include those constructed of or containing aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride and combinations thereof. When used, the inorganic filler component may be present in an amount within the range of about 5% by weight to about 95% by weight, desirably about 20% by weight to about 60% by weight, such as about 40% by weight of the total composition.

In addition, the composition may also include a flowability agent, such as a silane and/or titanate.

Appropriate silanes for use herein include octyl trimethoxy silane (commercially available from OSI Specialties Co., Danbury, Connecticut under the trade designation A-137), and methacryloxy propyl trimethoxy silane (commercially available from OSI under the trade designation A-174).

Appropriate titanates for use herein include titanium IV tetrakis [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0] [bis(ditridecylphosphito-0), dihydrogen]$_2$

(commercially available from Kenrich Petrochemical Inc., Bayonne, New Jersey under the trade designation KR-55).

When used, the flowability agent may be used in an amount of 0 to about 2 parts by weight, per 100 parts of the epoxy resin.

In addition, adhesion promoters, such as the silanes, glycidyl trimethoxysilane (commercially available from OSI under the trade designation A-187) or gamma-amino propyl triethoxysilane (commercially available from OSI under the trade designation A-1100), may be used.

Cyanate esters may also be used in the inventive compositions. The cyanate esters useful as a component in the inventive compositions may be chosen from dicyanatobenzenes, tricyanatobenzenes, dicyanatonaphthalenes, tricyanatonaphthalenes, dicyanato-biphenyl, bis(cyanatophenyl)methanes and alkyl derivatives thereof, bis(dihalocyanatophenyl)propanes, bis(cyanatophenyl)ethers, bis(cyanatophenyl)sulfides, bis(cyanatophenyl)propanes, tris(cyanatophenyl)phosphites, tris(cyanatophenyl)phosphates, bis(halocyanatophenyl)methanes, cyanated novolac, bis[cyanatophenyl(methylethylidene)]benzene, cyanated bisphenol-terminated thermoplastic oligomers, and combinations thereof.

More specifically, aryl compounds having at least one cyanate ester group on each molecule and may be generally represented by the formula $Ar(OCN)_m$, where Ar is an aromatic radical and m is an integer from 2 to 5. The aromatic radical Ar should contain at least 6 carbon atoms, and may be derived, for example, from aromatic hydrocarbons, such as benzene, biphenyl, naphthalene, anthracene, pyrene or the like. The aromatic radical Ar may also be derived from a polynuclear aromatic hydrocarbon in which at least two aromatic rings are

attached to each other through a bridging group. Also included are aromatic radicals derived from novolac-type phenolic resins -- i.e., cyanate esters of these phenolic resins. The aromatic radical Ar may also contain further ring-attached, non-reactive substituents.

Examples of such cyanate esters include, for instance, 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane; tris(4-cyanatophenyl)-phosphite; tris(4-cyanatophenyl)phosphate; bis(3-chloro-4-cyanatophenyl)methane; cyanated novolac; 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and cyanated bisphenol-terminated polycarbonate or other thermoplastic oligomer.

Other cyanate esters include cyanates disclosed in U.S. Patent Nos. 4,477,629 and 4,528,366, the disclosure of each of which is hereby expressly incorporated herein by reference; the cyanate esters disclosed in U.K. Pat. No. 1,305,702, and the cyanate esters disclosed in International Patent Publication WO 85/02184, the disclosure of each of which is hereby expressly incorporated herein by reference. Of course, combinations of these cyanate esters within the imidazole component of the compositions of the present invention are also desirably employed herein.

A particularly desirable cyanate ester for use herein is available commercially from Ciba Specialty

Chemicals, Tarrytown, New York under the tradename "AROCY" L10 [1,1-di(4-cyanatophenylethane)].

When used, the cyanate esters may be used in an amount of about 1 to about 20% by weight based on the total amount of the epoxy resin component.

Conventional additives may also be used in the compositions of the present invention to achieve certain desired physical properties of the composition, the cured reaction product, or both.

For instance, it may be desirable in certain instances (particularly where a large volume of inorganic filler component is used) to include a multifunctional epoxy resin reactive diluent, examples of which include those from Pacific Epoxy Polymers, under the trade designations PEP-6752 (trimethylolpropane triglycidyl ether) and PEP-6760 (diglycidyl aniline).

The thermosetting resin composition of the present invention may further contain other additives, such as defoaming agents, leveling agents, dyes and pigments. Moreover, photopolymerization initiators may also be incorporated therein, provided that such initiators do not adversely affect the properties of the composition or reaction products formed therefrom.

The thermosetting resin composition of the present invention may be formulated as a one-part composition, in which all the ingredients are mixed together, or as a two-part composition, in which the epoxy resin and the curing agent are stored separately and mixed thereafter prior to use. Accordingly, the curing agent used in the present invention can generally be any of the curing agents that are used in one-part and two-part epoxy resin formulations, particularly those noted above.

The thermosetting resin compositions according to the present invention are capable of penetrating into the space between the circuit board and the semiconductor device. These inventive compositions also demonstrate a reduced viscosity, at least under elevated temperature conditions, and thus are capable of penetrating into that space. It is desirable to prepare the thermosetting resin composition by selecting the types and proportions of various ingredients to reach a viscosity at 25°C of 10,000 mPa·s or less, such as 3,000 - 4,000 mPa·s, so as to improve its ability to penetrate into the space (e.g., of 50 to 500μm) between the circuit board and the semiconductor device.

Reference to FIG. 1 shows an example of a semiconductor device mounting structure, such as a CSP, in which the thermosetting resin composition of the present invention is used.

The semiconductor device 4 is one formed by connecting a semiconductor chip (so-called bare chip) 2, such as LSI, to a carrier substrate 1 and sealing the space therebetween suitably with resin 3. This semiconductor device is mounted at a predetermined position of the circuit board 5, and electrodes 8 and 9 are electrically connected by a suitable connection means such as solder. In order to improve reliability, the space between carrier substrate 1 and circuit board 5 is sealed with the cured product 10 of a thermosetting resin composition. The cured product 10 of the thermosetting resin composition need not completely fill the space between carrier substrate 1 and circuit board 5, but may fill it to such an extent as to relieve stresses caused by thermal cycling.

Carrier substrates may be constructed from ceramic substrates made of Al_2O_3, SiN_3 and mullite (Al_2O_3-SiO_2); substrates or tapes made of heat-resistant resins such as polyimides; glass-reinforced epoxy, ABS and phenolic substrates which are also used commonly as circuit boards; and the like.

As regards flip chip assemblies, reference to FIG. 3 shows a flip chip assembly in which a semiconductor chip has been mounted onto a circuit board, and the underfilling sealed with a thermosetting resin composition of the present invention.

The flip chip assembly 34 is formed by connecting a semiconductor chip (a bare chip) 32 to a circuit board 31 and sealing the space therebetween suitably with a thermosetting resin composition 33. This semiconductor device is mounted at a predetermined position on the circuit board 31 and electrodes 35 and 36 are electrically connected by a suitable electrical connection means 37 and 38, such as solder. In order to improve reliability, the space between the semiconductor chip 32 and the circuit board 31 is sealed with a thermosetting resin composition 33 and then cured. The cured product of the thermosetting resin composition should completely fill that space.

No particular limitation is placed on the means for electrically connecting the semiconductor chip to the carrier substrate, and there may be employed connection by a high-melting solder or electrically (or anisotropically) conductive adhesive, wire bonding, and the like. In order to facilitate connections, the electrodes may be formed as bumps. Moreover, in order to improve the reliability and durability of connections, the space between the semiconductor chip and the

carrier substrate may be sealed with a suitable resin. The semiconductor devices that can be used in the present invention include CSPs, BGAs, and LGAs.

No particular limitation is placed on the type of circuit board used in the present invention, and there may be used any of various common circuit boards such as glass-reinforced epoxy, ABS and phenolic boards.

Next, the mounting process is described below. Initially, cream solder is printed at the necessary positions of a circuit board and suitably dried to expel the solvent. Then, a semiconductor device is mounted in conformity with the pattern on the circuit board. This circuit board is passed through a reflowing furnace to melt the solder and thereby solder the semiconductor device. The electrical connection between the semiconductor device and the circuit board is not limited to the use of cream solder, but may be made by use of solder balls. Alternatively, this connection may also be made through an electrically conductive adhesive or an anisotropically conductive adhesive. Moreover, cream solder or the like may be applied or formed on either the circuit board or the semiconductor device. In order to facilitate subsequent repairs, the solder, electrically or anisotropically conductive adhesive used should be chosen bearing in mind its melting point, bond strength and the like.

After the semiconductor device is electrically connected to the circuit board in this manner, the resulting structure should ordinarily be subjected to a continuity test or the like. After passing such test, the semiconductor device may be fixed thereto with a resin composition. In this way, in the event of a failure, it is easier to remove the semiconductor device before fixing it with the resin composition.

Then, using a suitable application means such as dispenser, a thermosetting resin composition is applied to the periphery of the semiconductor device. When this composition is applied to the semiconductor device, it penetrates into the space between the circuit board and the carrier substrate of the semiconductor device by capillary action.

Next, the thermosetting resin composition is cured by the application of heat. During the early stage of this heating, the thermosetting resin composition shows a significant reduction in viscosity and hence an increase in fluidity, so that it more easily penetrates into the space between the circuit board and the semiconductor device. Moreover, by providing the circuit board with suitable venting holes, the thermosetting resin composition is allowed to penetrate fully into the entire space between the circuit board and the semiconductor device.

The amount of thermosetting resin composition applied should be suitably adjusted so as to fill the space between the circuit board and the semiconductor device almost completely.

When the above-described thermosetting resin composition is used, it is usually cured by heating at a temperature of about 80°C to about 150°C for a period of time of about 5 to about 60 minutes. Thus, the present invention can employ relatively low-temperature and short-time curing conditions and hence achieve very good productivity. The semiconductor device mounting structure illustrated in FIG. 1 is completed in this manner.

In the mounting process using the thermosetting resin composition of the present invention, after the semiconductor device is mounted on the circuit board as described above, the resulting structure is tested with

respect to characteristics of the semiconductor device, connection between the semiconductor device and the circuit board, other electrical characteristics, and the state of sealing. In the event a failure is found, repair can be made in the following manner.

The area around the semiconductor device that has failed is heated at a temperature of about 190°C to about 260°C for a period of time ranging from about 10 seconds to about 60 seconds. Although no particular limitation is placed on the heating means, local heating is preferred. There may be employed a relatively simple means such as the application of hot air to the failure site.

As soon as the solder is melted and the resin is softened to cause a reduction in bond strength, the semiconductor device is pulled apart.

After the semiconductor device 4 is removed as shown in FIG. 2, a residue 12 of the cured reaction product of the thermosetting resin composition and a residue 14 of the solder are left on the circuit board 5. The residue of the cured product of the thermosetting resin composition can be removed, for example, by scraping it off after the residue has been softened by heating it to a predetermined temperature, allowing it to swell with solvent, or allowing it to swell with solvent while heating it to a predetermined temperature.

The residue can be most easily removed by using both heating and solvent. For example, the residue can be scraped off after it has been softened by allowing the residual resin to swell with solvent while keeping the entire circuit board at a temperature of about 100°C (usually in the range of about 80°C to about 120°C).

The solvent used for this purpose is one which causes cured reaction products of the thermosetting resin

composition to swell, thereby reducing bond strength to such an extent that the cured material can be scraped off from the circuit board. Useful solvents include organic ones, for example, alkyl chlorides, such as methylene chloride; glycol ethers, such as ethyl cellulose and butyl cellulose; diesters of dibasic acids, such as diethyl succinate; and N-methylpyrrolidone. Of course, appropriate combinations may also be employed.

Where a circuit-protecting resist has already been connected to the circuit board, the chosen solvents should cause no damage to the resist. Desirable solvents with this in mind include glycol ethers and N-methylpyrrolidone.

The residue of the solder can be removed, for example, by use of a solder-absorbing braided wire.

Finally, on the circuit board which has been cleaned according to the above-described procedure, a new semiconductor device may be mounted again in the same manner as described previously. Thus, the repair of the failure site is completed.

Where a failure is found in the circuit board, the semiconductor device can be reused by removing the residue 13 of the cured reaction product of the thermosetting resin composition and the residue 15 of the solder left on the bottom of the semiconductor device in the same manner as described above. (See FIG. 4.)

The invention will be further illustrated by the following non-limiting examples.

EXAMPLES

Example 1

Thermosetting Resin Composition

A thermosetting resin compositions in accordance with the present invention may be prepared from the components as noted below in Tables 1a-1f.

Table 1a

Component		Sample No./Amt (grams)							
Type	Identity	1	2	3	4	5	6	7	8
Epoxy	BEO - 60E	61.176	42.824	36.706	--	--	--	--	--
	BPO - 20E	--	--	--	65.488	58.939	45.842	32.744	59.002
	DME - 100	--	--	--	--	--	--	--	--
Curing Agent	NOVACURE HX-3722	6.275	4.392	3.765.	--	--	--	--	6.254
Anhydride	MTA - 15	32.549	22.784	19.529	--	--	--	--	34.744
	MH - 700	--	--	--	32.417	29.175	22.692	16.208	--
Inorganic Filler	SO - E5	--	30	40	--	10	30	50	--

Table 1b

Component		Sample No./Amt (grams)							
Type	Identity	9	10	11	12	13	14	15	16
Epoxy	BEO - 60E	--	--	--	--	--	--	--	--
	BPO - 20E	41.301	35.402	--	--	--	--	--	--
	DME - 100	--	--	48.426	44.262	44.550	40.095	35.640	31.185
Curing Agent	NOVACURE HX-3722	4.378	3.752	--	6.246	5.750	5.175	4.600	4.025
	MY-24	--	--	2.082	--	--	--	--	--
Anhydride	MTA - 15	24.321	20.846	--	--	--	--	--	--
	MH - 700	--	--	49.492	49.492	48.700	43.830	38.960	34.090
Inorganic Filler	SO - E5	--	30	40	--	10	30	50	--

Table 1c

Component		Sample No./Amt. (grams)						
Type	Identity	17	18	19	20	21	22	23
Resin	MPG	47.80	45	54.05	48.65	43.24	--	--
	XBO	--	--	--	--	--	45.80	98
Curing Agent	NOVACURE HX-3722	6	55	2.7	2.43	2.16	6	--
	MH - 700 (Anhydride)	46.20	--	43.25	38.92	34.60	48.20	--
	SI 100 (Cationic Catalyst)	--	--	--	--	--	--	2
Inorganic Filler	SO-E5	--	--	--	10	20	--	--

For comparative purposes, Sample Nos. 24-30 were prepared substantially as Sample Nos. 17-23, save for the curable resin, which was replaced with a comparable amount of an epoxy resin -- either bisphenol-A-type epoxy resin or bisphenol-F-type epoxy resin. See Table 1d.

Table 1d

Component		Sample No./Amt. (grams)						
Type	Identity	24	25	26	27	28	29	30
Epoxy	Bisphenol A	45	48.42	43.58	38.74	--	--	--
	Bisphenol F	--	--	--	--	45	45.80	98
Curing Agent	NOVACURE HX-3722	55	6.32	5.68	5.05	55	6	--
	MH - 700 (Anhydride)	--	45.26	40.74	36.21	--	48.20	--
	SI 100 (Cationic Catalyst)	--	--	--	--	--	--	2
Inorganic Filler	SO-E5	--	--	10	20	--	--	--

Table 1e

Component		Sample No./Amt. (grams)								
Type	Identity	31	32	33	34	35	36	37	38	39
Resin	CBO	40	98	85.75	78.40	61.25	49	36.75	19.60	12.25
	RE403S	–	–	12.25	19.60	36.75	49	61.25	76.40	85.75
Curing Agent	NOVACURE HX-3722	6	–	–	–	–	–	–	–	–
	MH-700 (Anhydride)	54	–	–	–	–	–	–	–	–
	SI 100 (Cationic Catalyst)	–	2	2	2	2	2	2	2	2
Inorganic Filler	SO-E5	–	–	–	–	–	–	–	–	–

For comparative purposes, Sample Nos. 40-48 were prepared as Sample Nos. 31-39, save for the curable resin, which was replaced with a comparable amount of an epoxy resin -- either bisphenol-A-type epoxy resin or bisphenol-F-type epoxy resin. The comparative samples are presented in Table 1f.

Table 1f

Component		Sample No./Amt. (grams)								
Type	Identity	40	41	42	43	44	45	46	47	48
Epoxy	Bisphenol A	–	45	48.42	43.58	38.74	–	–	–	–
	Bisphenol F	98	–	–	–	–	45	46	41.40	36.80
Curing Agent	NOVACURE HX-3722	–	55	6.32	5.68	5.05	55	6	5.40	4.80
	MH-700 (Anhydride)	–	–	45.26	40.74	36.21	–	48	10	20
	SI 100 (Cationic Catalyst)	2	–	–	–	–	–	–	–	–
Inorganic Filler	SO-E5	–	–	–	10	20	–	–	10	20

Table 1g

Comp nent		Sample No./Amt (grams)		
Type	Identity	49 (range)	50	51
Epoxy	Bisphenol A	–	–	51.4
	Bisphenol F	48.83 - 53.97	51.4	–
Curing Agent	ANCAMINE 2337S	34.49 - 38.12	36.3	36.3
Coreactant	Glycidyl neodecanoate	11.69 - 12.92	12.3	12.3

Physical Properties

In the uncured state, the compositions were observed to have the viscosity values in mPa·s as set forth in Table 2.

In the cured state, reaction products of the composition were observed to have a glass transition temperature ("Tg") as measured by thermal mechanical analysis ("TMA"), α_1 and α_2, and expansion when cycled between extreme temperatures of about 0°C and about 140°C as set forth in Tables 2a-2d.

Table 2a

Sample No.	Physical Properties				
	Visc. (mPa·s)	Tg (°C)	α_1	α_2	Expansion (mm)
1	1838	50.50	69.34	179.96	0.190
2	4534	50.12	53.20	150.14	0.160
3	8671				
4	1047	66.25	64.28	188.36	0.180
5	1342	69.24	59.66	179.84	0.175
6	2521	67.36	49.26	159.2	0.175
7	13450	68.4	36.3	136.7	0.150
8	5303	84.86	60.16	180.00	0.160
9	12110	--	--	--	--
10	21960	--	--	--	--
11	70	--	--	--	--
12	63	90.82	65.84	175.92	0.165
13	75	83.17	65.40	180.28	0.160
14	95	87.14	59.71	174.56	0.160
15	133	84.33	56.00	159.20	0.135
16	167	87.61	49.12	147.07	0.135

Table 2b

Sample No.	Physical Properties				
	Visc. (mPas)	Tg (°C)	α_1	α_2	Adhesion Strength (N/mm^2)
17	--	--	--	--	--
18	3108	66.40	57.78	182.37	21.30
19	147.9	107.57	58.92	170.23	3.71
20	191.2	108.34	51.78	164.45	3.13
21	259.9	111.19	48.04	152.56	2.94
22	152.2	--	--	--	--
23	--	--	--	--	--
24	33490	121.61	57.12	196.61	22.61
25	815.6	132.31	59.62	182.99	4.42
26	2155	148.2	52.63	167.86	4.29
27	2585	140.86	54.79	156.27	3.57
28	334.5	119.12	58.57	172.14	5.51
29	752.9	126.89	52.83	156.27	4.77
30	315.6	127.35	49.59	163.54	--

Table 2c

Sample No.	Physical Properties				
	Visc. (mPa.s)	Tg (°C)	α_1	α_2	Adhesion Strength (N/mm^2)
31	12.20	--	--	--	--
32	43.68	-0.91	64.31	175.63	--
33	--	--	--	--	--
34	78.06	22.91	66.62	184.26	--
35	--	--	--	--	--
36	132.50	40.42	69.21	183.22	--
37	--	--	--	--	--
38	146.1	31.12	54.37	185.54	--
39	--	--	--	--	--
40	315.6	127.35	49.59	163.54	--
41	33490	121.61	57.12	196.61	22.61
42	815.6	132.31	59.62	182.99	4.42
43	2155	148.2	54.79	161.96	4.29
44	2585	140.86	52.63	156.27	3.57
45	334.5	119.12	58.57	172.14	5.51
46	15420	120.11	55.49	182.84	20.94
47	752.9	126.87	52.83	167.86	4.77
48	892.4	129.62	48.5	157.82	4.27

Table 2d

Sample No.	Physical Properties				
	Visc. (mPas)	Tg (°C)	α_1	α_2	Modulus (N/mm^2)
50	4000	41	60	195	5400
51	8000	--	--	--	--

The viscosity of the majority of these samples is suitable for use as an underfill sealant. That is, a viscosity less than about 10,000 mPa·s. The Tg values for the samples listed are suitable for use as an underfill sealant. Though not given in any of Tables 2a-2d, the coefficient of thermal expansion values for the samples were between about 0°C and about 140°C, which is suitable for use as an underfill sealant.

Mounting Process

Using cream solder (PS10R-350A-F92C; manufactured by Harima Chemicals, Inc.), a CSP having a package of 10mm square, an electrode diameter of 0.5mm, an electrode pitch of 1.0mm, and a carrier substrate made of alumina was mounted on a 1.6mm thick glass-reinforced epoxy board having a circuit formed thereon.

Thereafter, the thermosetting resin composition was applied to the periphery of the CSP by means of a dispenser, and then cured by heating in an environment where the temperature was held at about at 150°C for a period of time of about 60 minutes. The thermosetting resin composition penetrated into the space between the semiconductor device and the circuit board before curing completely.

Heat Shock Test

Four replicates of Sample Nos. 2 and 8 prepared as described above were exposed to a heat shock test while maintaining the replicates at a temperature of about -40°C for a period of time of about 10 minutes and thereafter an elevation of temperature to about +125°C for a period of time of about 10 minutes. After a predetermined number of thermal cycles were reached, the replicates were subjected to a continuity test to confirm the electrical connection between the CSP and the circuit board. The replicates were regarded as acceptable when continuity was confirmed to be at least 800 cycles, and unacceptable when continuity was lost owing to broken lines or the like before this number of cycles was reached. As to the mounting structure of this example, all of the replicates were acceptable even at more than 900 cycles.

Repair

Using a hot air generator, the area around the CSP fixed to the circuit board with the thermosetting resin composition as described above was heated by applying hot air at 250°C for 1 minute. Then, the CSP could be easily removed by inserting a metal piece between the CSP and the glass-reinforced epoxy board, and lifting the CSP.

While the glass-reinforced epoxy board was kept at a temperature of about 100°C by placing it on a hot plate (or by heating it with a far-infrared heater or the like), the resin left on the glass-reinforced epoxy board was allowed to swell with a solvent such as PS-1 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) or 7360 (manufactured by Loctite Corporation), and then scraped off with a spatula. The solder left on the glass-reinforced epoxy board was removed by use of a solder-absorbing braided wire. Residual trace resin

remaining on the glass-reinforced epoxy board was removed with acetone absorbed onto a cloth. The time required for this repairing operation was within about 3 minutes, which was sufficiently short from a practical point of view.

The ease of repair and reworkability of the cured adhesive is expressed below in Tables 3a-3d on a relative scale between 1 and 5, with 1 being an unreworkable cured adhesive and therefore incapable of repair and 5 being a reworkable cured adhesive and therefore easily repairable using the procedure described.

Table 3a

Sample No.	Reworkability	
	Heat	Acetone
1	4	3
2	3	3
3	2	--
4	4	4
5	4	3
6	3	3
7	3	3
8	4	3
9	2	--
10	2	--
11	5	--
12	5	--
13	4	3
14	4	4
15	3	3
16	3	3

Table 3b

Sample No.	Repairability/ Heat
17	--
18	3.5
19	3
20	2
21	2
22	--
23	--
24	1
25	2
26	1
27	1
28	2
29	1
30	2

Reference to FIG. 5 shows the temperature range at which a cured reaction product of a XBO-based composition curable through a cationic cure mechanism (Sample No. 23) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin curable through a cationic cure mechanism (Sample No. 30).

Reference to FIG. 6 shows the temperature range at which a cured reaction product of a MPG-based composition (Sample No. 17) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin (Sample No. 29).

Table 3c

Sample No.	Repairability/ Heat
31	--
32	5
33	--
34	4
35	--
36	3.5
37	--
38	3.5
39	--
40	2
41	1
42	2
43	1
44	1
45	1
46	2
47	1
48	1

Reference to FIG. 7 shows the temperature range at which a cured reaction product of a CBO-based composition curable through a cationic cure mechanism (Sample No. 32) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin curable through a cationic cure mechanism (Sample No. 40).

Table 3d

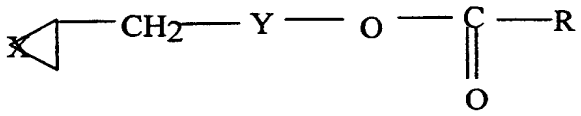
Sample No.	Repairability/ Heat
50	3.5
51	3

The full scope of the invention is measured by the claims.

What Is Claimed Is:

1. A thermosetting resin composition, reaction products of which are controllably degradable, said composition comprising:

(a) a curable resin component selected from the group consisting of curable resins having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one ether, thioether or carbonate linkage that is capable of degrading upon exposure to elevated temperature conditions and/or acidic conditions, epoxy resins, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group and the combination of an epoxy resin and a coreactant diluent represented by the structure:



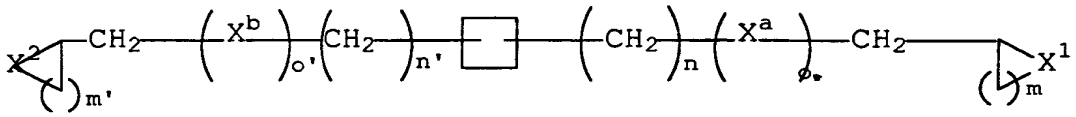
wherein X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents alkyl, alkenyl, and aryl; and R represents alkyl, alkenyl, and aryl; and

(b) a curing agent component.

2. The composition of Claim 1, further comprising an anhydride component.

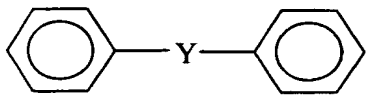
3. The composition of Claim 1, further comprising an inorganic filler component.

4. The composition of Claim 1, wherein the curable resin component is represented by the following structure:



wherein the box represents one or more aromatic ring(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms; X^1, X^2 X^a, and X^b may be the same or different and represent oxygen and sulfur; m and m^1 represent integers within the range of 1 to 3; n and n^1 represent integers within the range of 0 to 8; and o and o^1 represent integers within the range of 1 to 3.

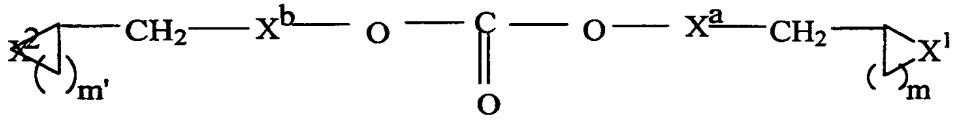
5. The composition of Claim 4, wherein the box is represented by



wherein Y may or may not be present, and where present a member selected from the group consisting of carbon, oxygen, sulfur, and phenylene.

6. The composition of Claim 4, wherein the box represents a structural linkage selected from the group consisting of individual aromatic rings, oligomeric systems and aromatic ring systems having multiple aromatic units joined in fused ring systems, joined in bi-aryl ring systems, bis-aryl ring systems, or cycloalaphatic-aromatic hybrid ring systems.

7. The composition of Claim 1, wherein the curable resin component is represented by the following structure:

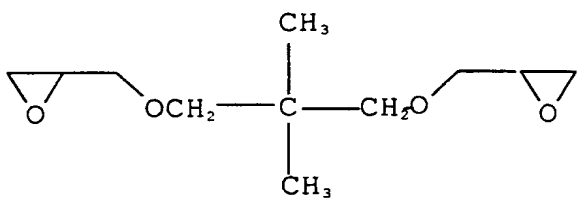


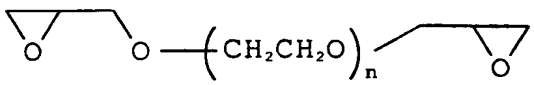
wherein X^1 and X^2 may be the same or different and represent oxygen and sulfur; X^a and X^b may be the same or different, may or may not be present, and represent alkyl, alkenyl, and aryl of one to about twenty carbon atoms, or one or more aromatic ring(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms; and m and m^1 represent integers within the range of 1 to 3.

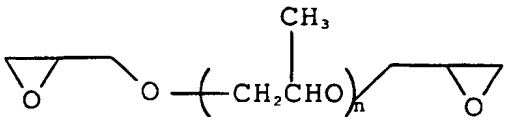
8. The composition of Claim 1, wherein the curable resin component is a member selected from the group consisting of MPG [bis[4-(2,3-epoxy-propylthio)phenyl]-sulfide], XBO [xylene bisoxetane], CBO (carbonate bisoxetane), and combinations thereof.

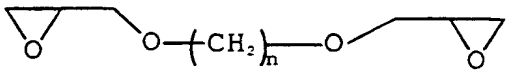
9. The composition of Claim 1, wherein the epoxy resin component includes mono- or multi-functional aliphatic epoxies, epoxies with a cycloaliphatic ring structure or system, or epoxies with an aromatic ring structure or system, and combinations thereof.

10. The composition of Claim 1, wherein the epoxy resin component includes

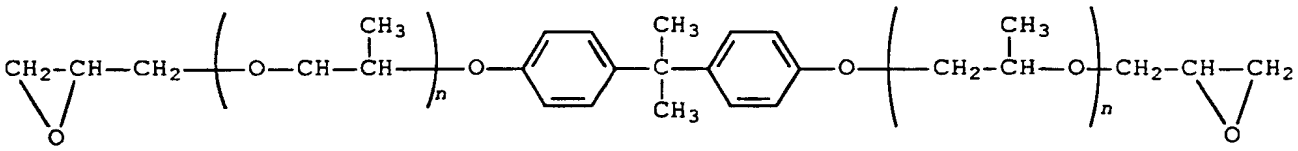


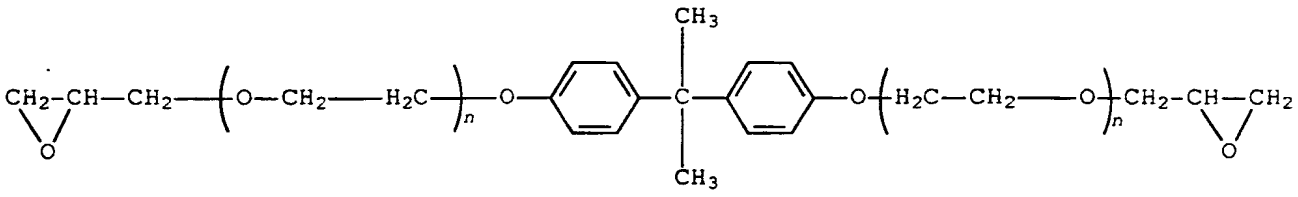




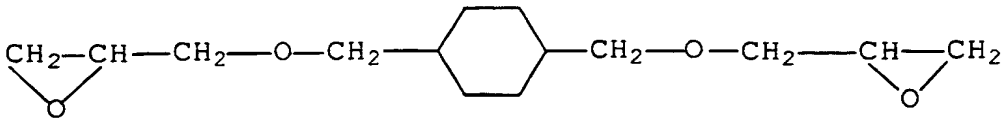


wherein n is an integer from 1 to about 18,



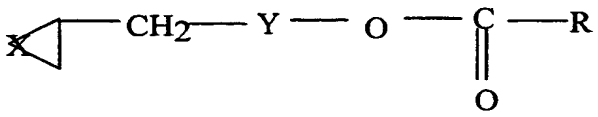


wherein n is as defined above,



and combinations thereof.

11. The composition of Claim 1, wherein the coreactant diluent is represented by the structure:



wherein X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents a linkage selected from the group consisting of linear, branched, cyclo or bicyclo alkyl or alkenyl of from one or two, respectively, to about twenty carbon atoms, and aryl of one or more aromatic ring(s) or ring system(s) of from about six to about twenty carbon atoms.

12. The composition of Claim 1, wherein the coreactant diluent is glycidyl neodecanoate.

13. The composition of Claim 1, wherein the curing agent component is a member selected from the group consisting of amine compounds, amide compounds, imidazole compounds, and derivatives and combinations thereof.

14. The composition of Claim 13, wherein the amine compounds are selected from the group consisting of aliphatic polyamines, aromatic polyamines, alicyclic polyamines and combinations thereof.

15. The composition of Claim 13, wherein the amine compounds are selected from the group consisting of diethylenetriamine, triethylenetetramine, diethylaminopropylamine, xylenediamine, diaminodiphenylamine, isophoronediamine, menthenediamine and combinations thereof.

16. The composition of Claim 13, wherein the amide compounds include cyano-functionalized amides.

17. The composition of Claim 13, wherein the imidazole compounds are selected from imidazole, isoimidazole, alkyl-substituted imidazoles, and combinations thereof.

18. The composition of Claim 13, wherein the imidazole compounds are selected from 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole and addition products of an imidazole and trimellitic acid, 2-n-heptadecyl-4-methylimidazole, aryl-substituted imidazoles, phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, 2-(2-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-naphthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-methoxystyrylimidazole, and combinations thereof.

19. The composition of Claim 13, wherein the modified amine compounds include epoxy amine additives formed by the addition of an amine compound to an epoxy compound.

20. The composition of Claim 13, wherein the modified amine compounds include "ANCAMINE" 2337S.

21. The composition of Claim 13, wherein the modified amine compounds are novolac-type resin modified through reaction with aliphatic amines.

22. The composition of Claim 13, wherein the modified imidazole compounds include imidazole adducts formed by the addition of an imidazole compound to an epoxy compound.

23. The composition of Claim 2, wherein the anhydride component is a member selected from the group consisting of hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, and combinations thereof.

24. The composition of Claim 3, wherein the inorganic filler component is a member selected from the group consisting of silica, aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride and combinations thereof.

25. A thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is

electrically connected, or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, reaction products of which are capable of softening and losing adhesivensss comprising:

a curable resin component as set forth in Claim 1 in an amount in the range of from about 20% by weight to about 60% by weight, a curing agent component in an amount within the range of from about 1 to about 10% by weight, and optionally an anhydride component in an amount within the range of from about 10 to about 60% by weight, and optionally an inorganic filler component in an amount up to about 60% by weight.

26. Reaction products of the compositions in accordance with any one of Claims 1-25.

27. An electronic device comprising a semiconductor device and a circuit board to which said semiconductor device is electrically connected or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, assembled using a thermosetting resin composition according to any one of Claims 1-25 as an underfill sealant between the semiconductor device and the circuit board or the semiconductor chip and the circuit board, respectively, wherein reaction products of the composition are capable of softening and losing their adhesiveness under exposure to temperature conditions in excess of those used to cure the composition.

28. A method of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said

semiconductor device is electrically connected or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, the steps of which comprise:

(a) dispensing into the underfilling between the semiconductor device and the circuit board or the semiconductor chip and the circuit board a composition in accordance with any one of Claims 1-25; and

(b) exposing the composition as so dispensed to conditions appropriate to cause the composition to form a reaction product.

29. A method of reworking a reaction product of a composition in accordance with any one of Claims 1-25, a step of which comprises:

(a) exposing the reaction product to conditions appropriate to cause the reaction product to soften and lose adhesiveness.

30. The method according to Claim 29, further comprising the steps of:

(b) removing the semiconductor chip or semiconductor device from the circuit board; and

(c) optionally, cleaning the surface of the circuit board to remove any cured reaction product that remains.

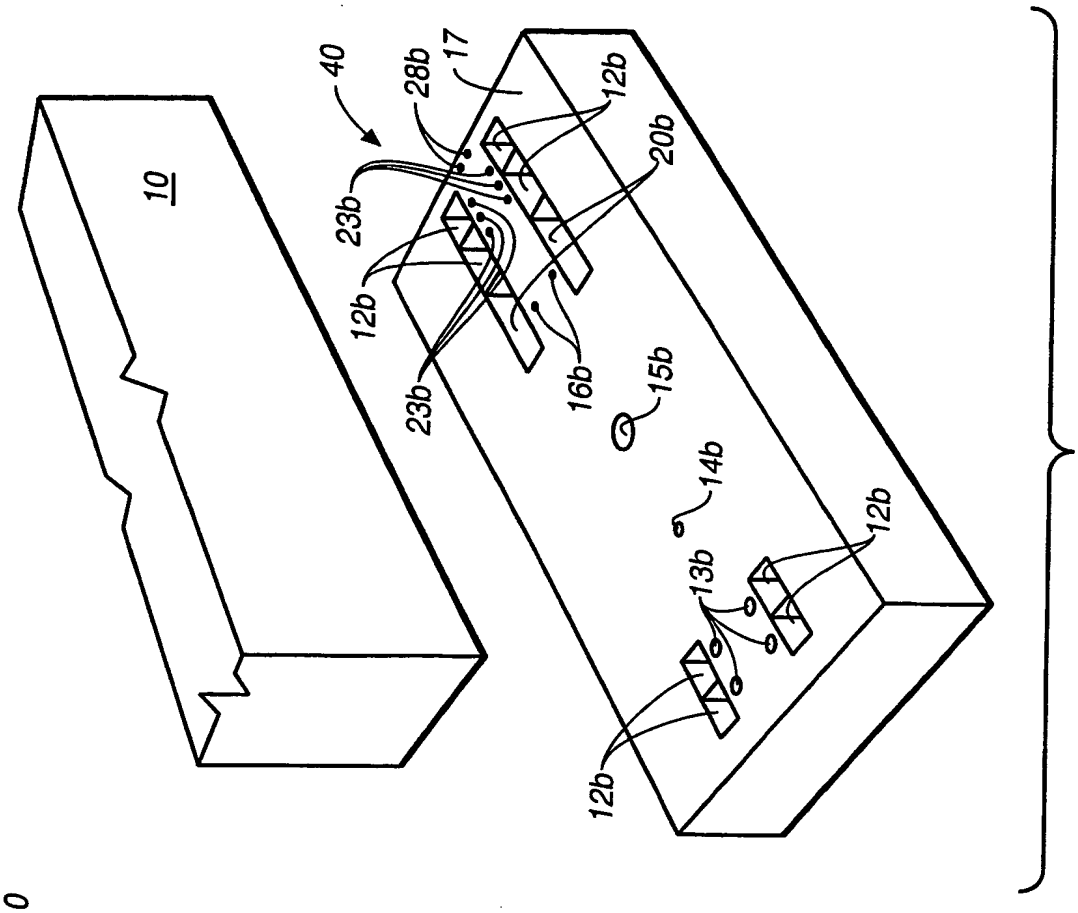

10
40
28b
17
12b
20b
23b
12b
16b
15b
14b
13b
12b
12b
23b

FIG._2

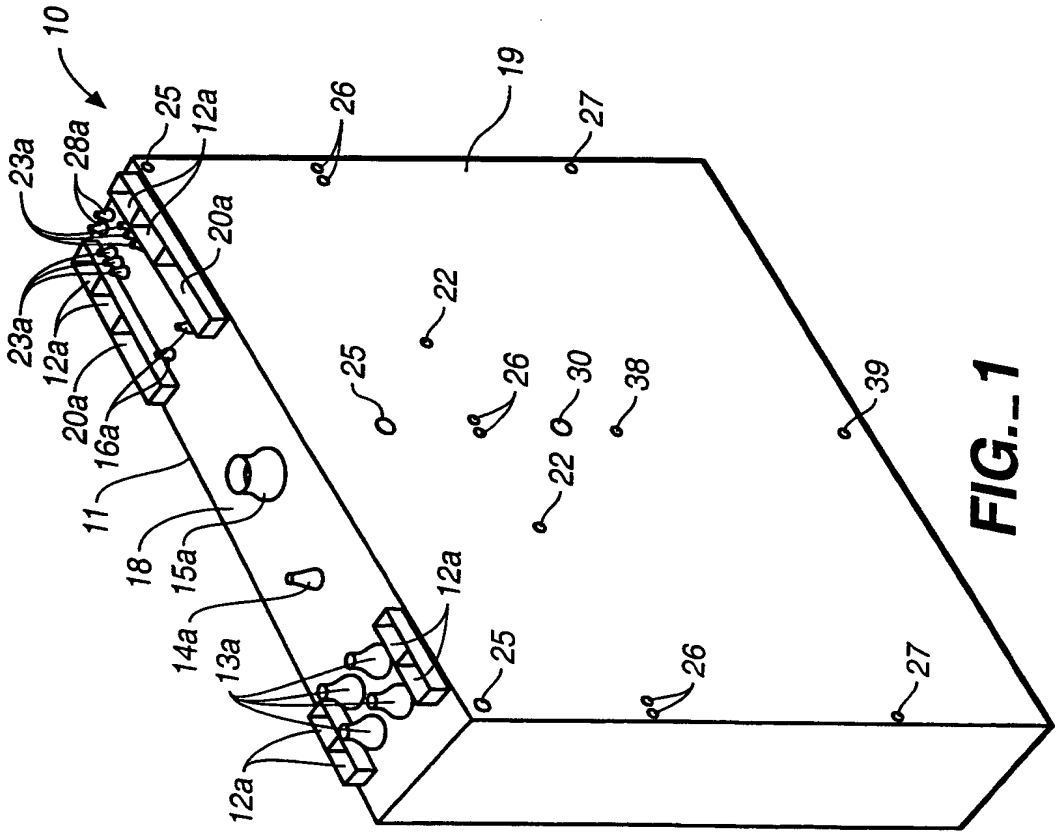
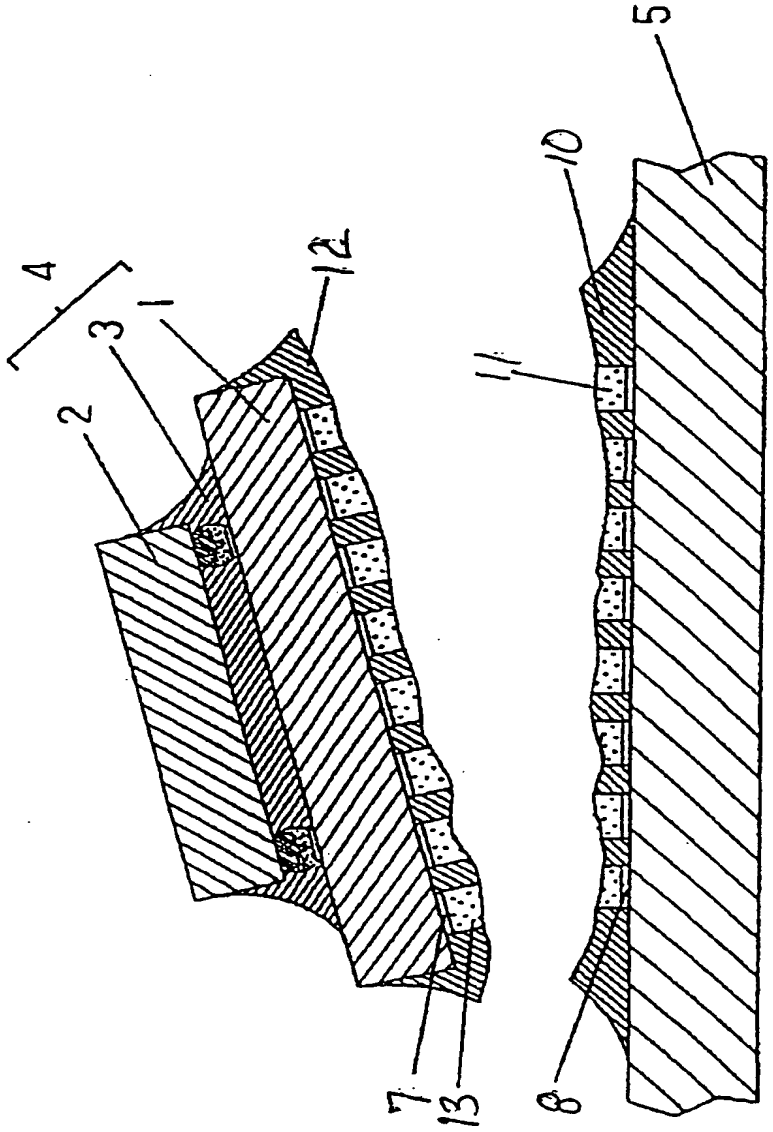

10
23a
28a
25
12a
26
19
27
20a
22
25
26
30
38
39
22
11
18
15a
14a
13a
12a
25
26
27
12a
23a
12a
20a
16a

FIG._1

FIG. 2



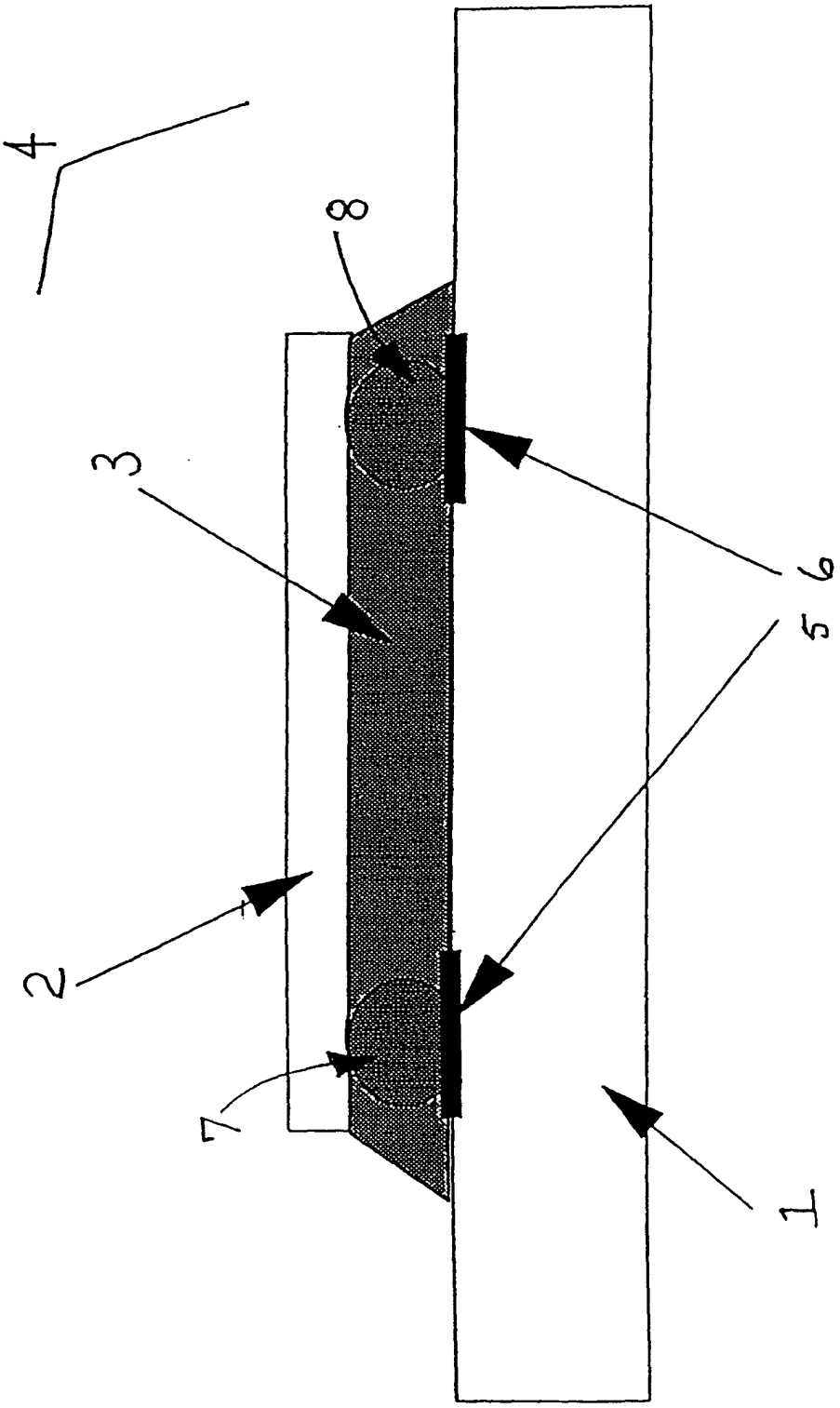


FIG. 3

FIG. 4

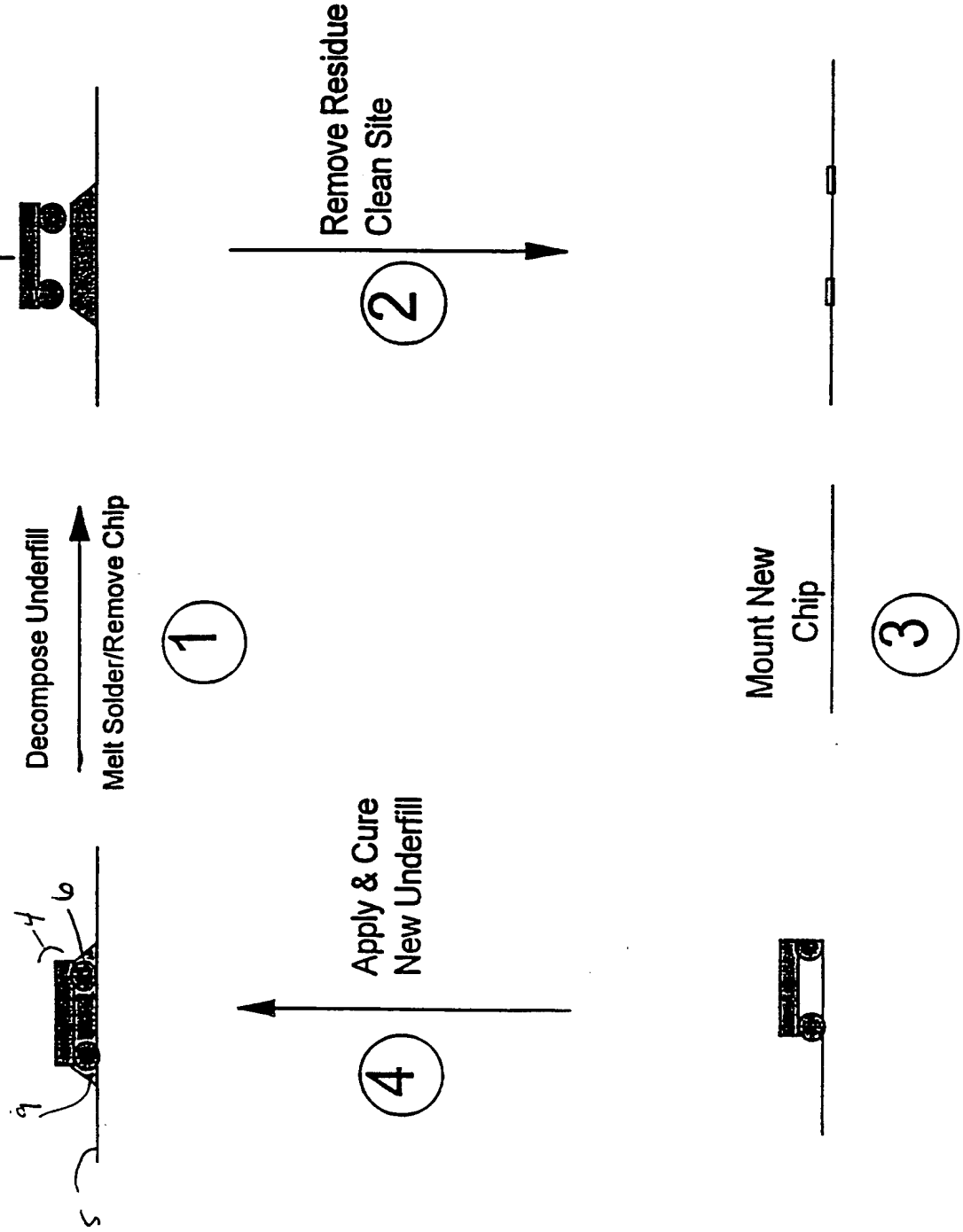

Reworkable Underfill Process Flow
Decompose Underfill
Melt Solder/Remove Chip
1
Remove Residue
Clean Site
2
Mount New
Chip
3
Apply & Cure
New Underfill
4
9
4
6
5

FIG. 5

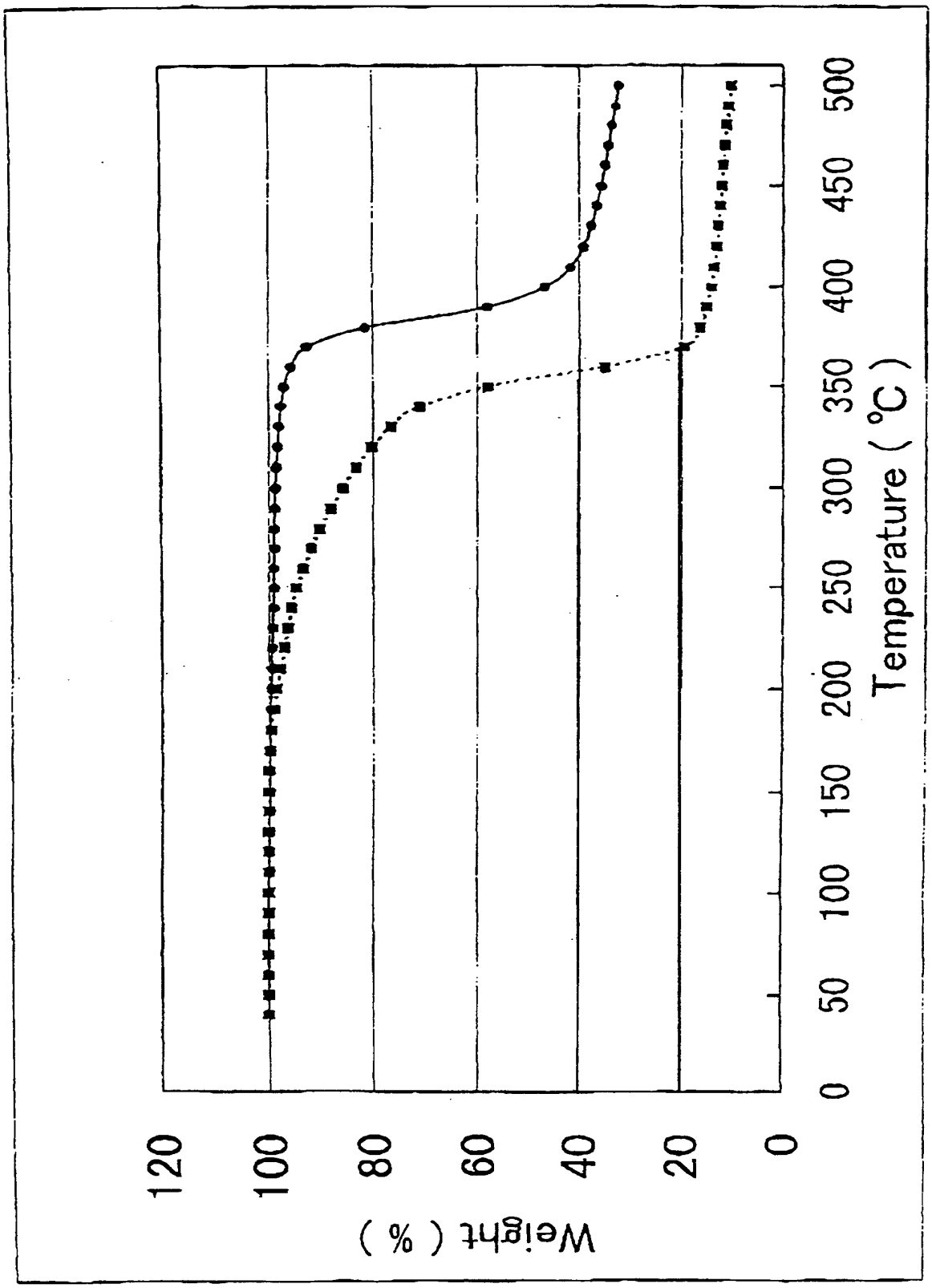

Weight (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

FIG. 6

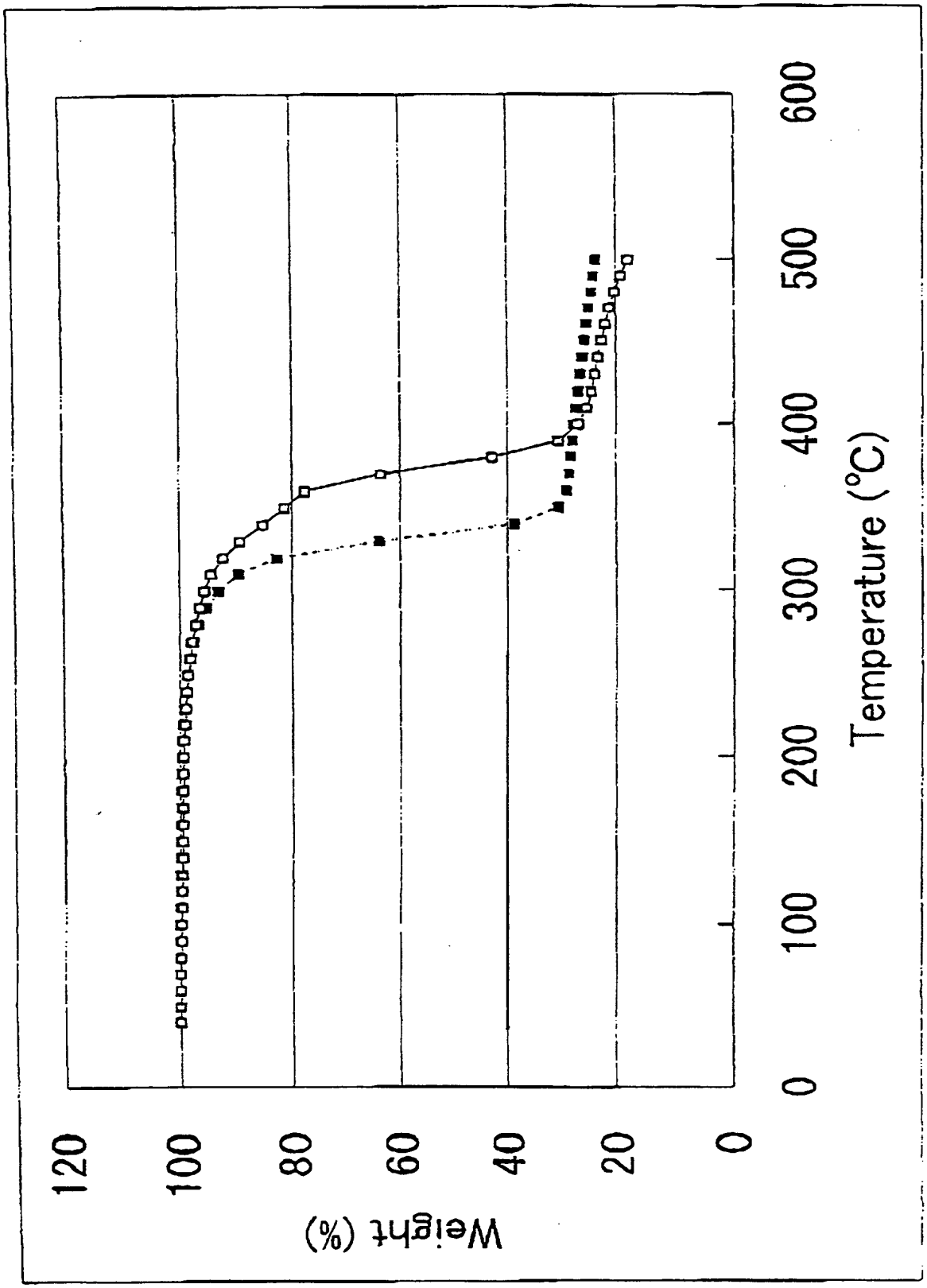

Weight (%)
120
100
80
60
40
20
0
0
100
200
300
400
500
600
Temperature (°C)

FIG. 7

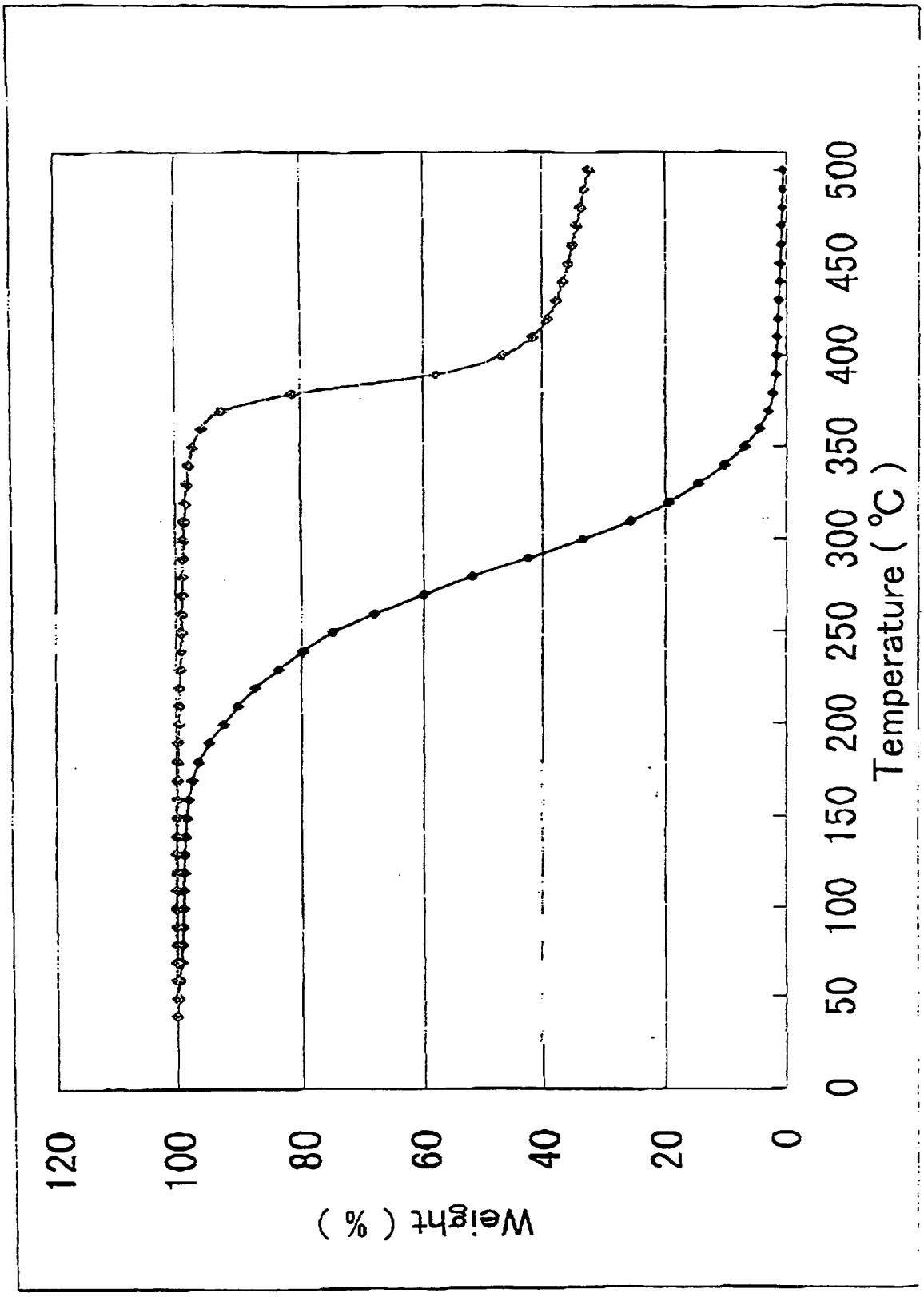

Weight (%)
120
100
80
60
40
20
0
0 50 100 150 200 250 300 350 400 450 500
Temperature (°C)

FIG. 8

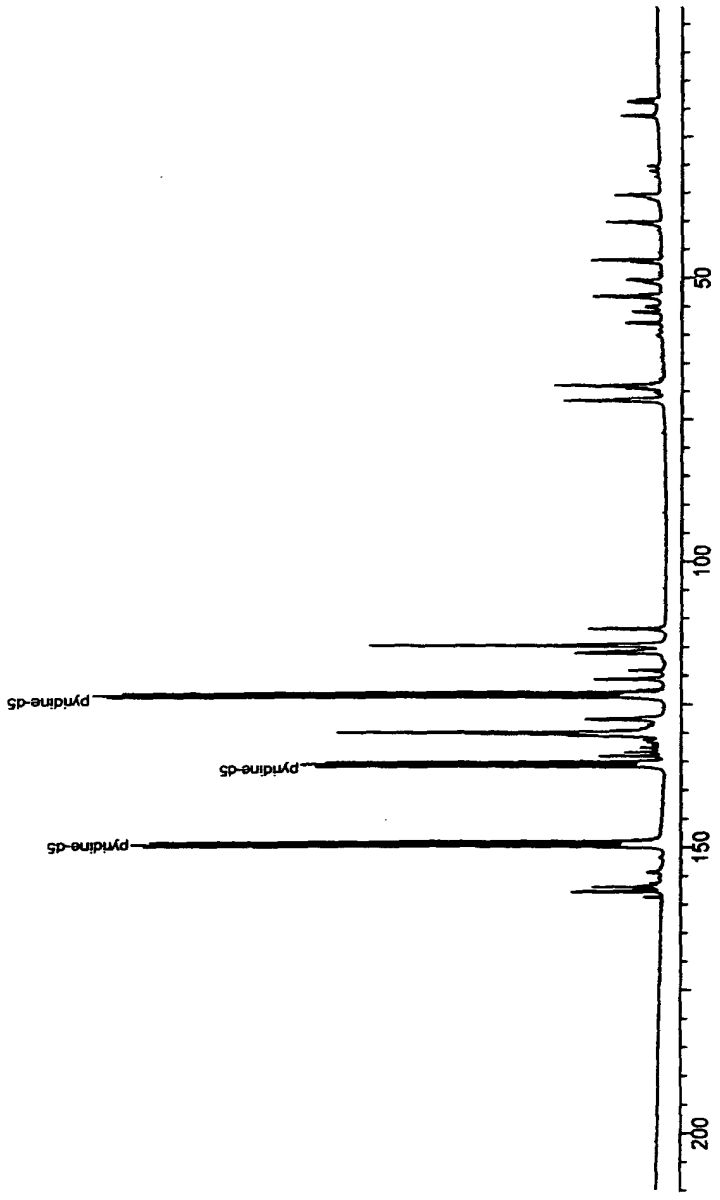
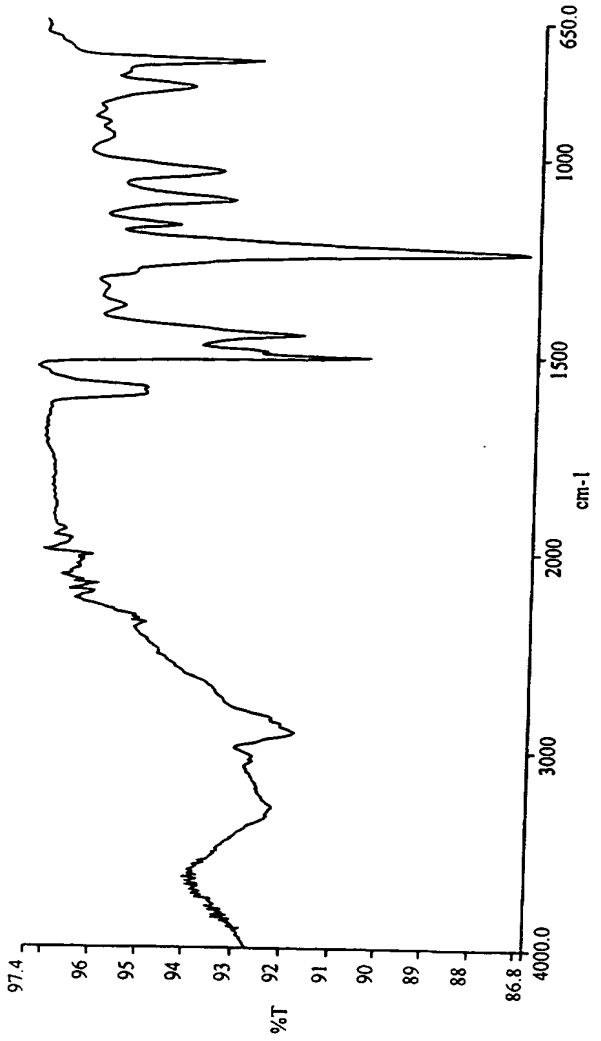


FIG. 9


650.0
1000
1500
2000
3000
4000.0
cm-1
97.4
96
95
94
93
92
91
90
89
88
86.8
%T

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,512,613 A (AFZALI-ARDAKANI et al.) 30 April 1996, columns 9-10, Example 7 and column 14, Example 23.	1-3, 13, 17, 18 and 23-30
Y,P	US 5,932,682 A (BUCHWALTER et al.) 03 August 1999, column 9, Example 2B and column 10, Examples 6 and 7.	1-3, 13, 17, 18 and 23-30
Y,P	US 6,008,266 A (KUCZYNSKI et al.) 28 December 1999, columns 11-12, Examples 1A and 1B.	1, 3 and 24-30
Y	JP 11-17074 A (JSR CO., LTD., JAPAN) 26 June 1997, abstracts.	1, 3 and 24-30
Y	JP 08-12741 A (NEW JAPAN CHEM CO LTD) 16 January 1996, abstract.	1-3 and 24-30

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 SEPTEMBER 2000	01 NOV 2000

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ROBERT SELLERS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 09-316421 A (SUMITOMO SEIKA K. K., JAPAN) 09 December 1997, abstract.	1
Y	JP 58-42290 A (HITACHI CHEMICAL CO., LTD., JAPAN) 03 November 1983, abstract.	1, 3 and 10
Y	JP 05-271389 A (TAIRU MENTO KK, JAPAN) 19 October 1993, abstracts.	1, 3, 10 and 24-30
Y	JP 02-18412 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 22 January 1990, abstracts.	1, 10, 13 and 24-30
Y	JP 63-159426 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 02 July 1988, abstract.	1-3 and 10
Y	JP 62-295029 A (HITACHI LTD., JAPAN) 22 December 1987, abstract.	1, 3, 10, 13, 17 and 18
Y	JP 06-136092 A (NEW JAPAN CHEM CO LTD) 17 May 1994, abstract.	1 and 10
Y	SERGEEV et al. Diglycidyl aromatic thio ethers and epoxy polymers derived from them. Vysokomol. Soedin., 1984, Vol. 26, No. 1, pages 208-211, abstract.	4-6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN-CAS: Files REG and CAPLUS. Search terms: Registry numbers for curable resin species disclosed on pages 11, 15 and 31 of the descrption. WEST: Files USPT, DWPI, JPAB, EPAB and IBM. Search terms: oxyalkylated epoxy resins, underfilling sealing, reworkable.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-26 and 28, drawn to a thermosetting resin composition and a method of sealing underfilling between a semiconductor device and a circuit board.
Group II, claims 1-26, 29 and 30, drawn to a thermosetting resin composition and a method of reworking a reaction product of the composition.
Group III, claim 27, drawn to an electronic device.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. The special technical feature is the composition of curable resin and a curing agent which is set forth in KUCZYNAKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The claimed composition does not make a contribution over the prior art, thereby establishing a lack of unity.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

1) The curable resins (a) of claims 4-12 comprising:
   i) Curable resins with a (thio)ether or carbonate core structure and pendant heteroatom-containing carbocyclic structures.
   ii) Alkylene oxide-containing epoxy resins.
   iii) An epoxy resin and a monoepoxy (thio)ester or carbonate coreactant diluent.

2) The curing agents (b) including amine compounds, amide compounds, imidazole compounds and their derivatives.

3) The compositions with and without the anhydride component.

The claims are deemed to correspond to the species listed above in the following manner:

1) Curable resins (a): Claims 4-12.
2) Curing agents (b): Claims 13-22.
3) Anhydride: Claims 2 and 23.

Claims 1-30 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features. The special technical feature is the composition of curable resin (a) and curing agent (b) which is disclosed in KUCZYNSKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The composition does not make a contribution over the prior art, thereby establishing a lack of unity between

the species.

The examination of all inventions and species has been elected.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 December 2000 (28.12.2000)

PCT

(10) International Publication Number
WO 00/79582 A1

(51) International Patent Classification[7]: H01L 21/56, 21/58, C08K 3/36, C08L 63/00, 69/00, 71/00

(21) International Application Number: PCT/US00/11878

(22) International Filing Date: 16 June 2000 (16.06.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/139,486	17 June 1999 (17.06.1999)	US
60/193,392	31 March 2000 (31.03.2000)	US
60/193,391	31 March 2000 (31.03.2000)	US
60/210,470	9 June 2000 (09.06.2000)	US

(71) Applicants *(for all designated States except US)*: **LOCTITE CORPORATION** [US/US]; Legal Dept., 1001 Trout Brook Crossing, Rocky Hill, CT 06067 (US). **LOCTITE (JAPAN) CORPORATION** [JP/JP]; 15-13, Fukuura 1-chome, Kanazawa-ku, Yokohama 236 (JP).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **DOBA, Takahisa** [JP/JP]; 3-18-7, Noukendai, Kanazawa-ku, Yokohama 236-0057 (JP).

(74) Agent: **BAUMAN, Steven, C.**; Loctite Corporation, 1001 Trout Brook Crossing, Rocky Hill, CT 06067 (US).

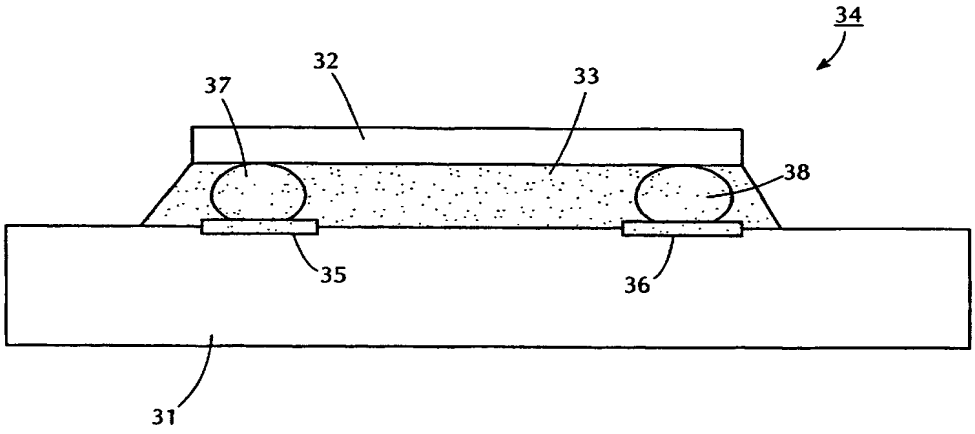
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

[Continued on next page]

(54) Title: CONTROLLABLY DEGRADABLE COMPOSITION OF HETEROATOM CARBOCYCLIC OR EPOXY RESIN AND CURING AGENT



(57) Abstract: A reworkable underfilling sealing mateiral (33) for the attachment of a semiconductor device (32) to a carrier substrate (31) is prepared from a composition comprising a curable resin (a) which is a resin with a (thio)ether or carbonate core structure and a heteroatom-containing carbocyclic structure, an epoxy resin having at least one alkylene oxide residue, or an epoxy resin with a monepoxide (thio)ester or carbonate coreactant diluent; and (b) a curing agent including a polyamine, an epoxy- or novolac-modified amine, an amide compound or an imidazole; optionally with an anhydride.

WO 00/79582 A1

(48) **Date of publication of this corrected version:**
15 March 2001

(15) **Information about Correction:**
see PCT Gazette No. 11/2001 of 15 March 2001, Section II

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

REWORKABLE THERMOSETTING RESIN COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to thermosetting resin compositions useful for mounting onto a circuit board semiconductor devices, such as chip size or chip scale packages ("CSPs"), ball grid arrays ("BGAs"), land grid arrays ("LGAs") and the like, each of which having a semiconductor chip, such as large scale integration ("LSI"), on a carrier substrate. Similarly, the compositions are useful for mounting onto circuit board semiconductor chips themselves. Reaction products of the compositions of this invention are controllably reworkable when subjected to appropriate conditions.

Brief Description of Related Technology

In recent years, the popularity of small-sized electronic appliances, such as camera-integrated video tape recorders ("VTRs") and portable telephone sets, has made size

reduction of LSI devices desirable. As a result of these reduction desires, CSPs, BGAs and LGAs are being used to reduce the size of packages substantially to that of bare chips. Such CSPs, BGAs and LGAs improve the characteristics of the electronic device while retaining many of their operating features, thus serving to protect semiconductor bare chips, such as LSIs, and facilitate testing thereof.

Ordinarily, the CSP/BGA/LGA assembly is connected to electrical conductors on a circuit board by use of a solder connection or the like. However, when the resulting CSP/BGA/LGA/circuit board structure is exposed to thermal cycling, vibration, distortion or is dropped, the reliability of the solder connection between the circuit board and the CSP/BGA/LGA often becomes suspect. Recently, after a CSP/BGA/LGA assembly is mounted on a circuit board, the space between the CSP/BGA/LGA assembly and the circuit board is often now filled with a sealing resin (commonly referred to as underfill sealing) in order to relieve stresses caused by thermal cycling, thereby improving heat shock properties and enhancing the reliability of the structure.

However, since thermosetting resins that form cross linked networks when cured are typically used as the underfill sealing material, in the event of a failure after the CSP/BGA/LGA assembly is mounted on the circuit board, it is difficult to replace the CSP/BGA/LGA assembly without destroying or scrapping the CSP/BGA/LGA assembly-circuit board structure in its entirety.

To that end, techniques for mounting a semiconductor chip on a circuit board are accepted as substantially similar to the mounting of a CSP/BGA/LGA assembly onto a circuit board. One such technique, disclosed in Japanese Laid-Open Patent Publication No. 102343/93, involves a mounting process

where a semiconductor chip is fixed and connected to a circuit board by use of a photocurable adhesive. In the event of failure, this semiconductor chip is removable. However, this technique requires the circuit board to be a transparent substrate (e.g., glass) which permits exposure to light from the back side. Since the circuit board is constructed of such a substrate, the resulting structure often exhibits poor heat shock resistance.

Japanese Laid-Open Patent Publication No. 69280/94 discloses a process where a semiconductor chip is fixed and connected to a substrate by use of a resin capable of hardening at a predetermined temperature. In the event of failure, the semiconductor chip is removed from the substrate by softening the resin at a temperature higher than the predetermined temperature. No specific resin is disclosed, and there is no discussion regarding treating the resin that remains on the substrate. Thus, the disclosed process is at best incomplete.

As pointed out in U.S. Patent No. 5,423,931 (Inoue), it is conventional to use a solvent to remove residual resin from a circuit board. However, swelling the resin with a solvent is a time-consuming process and the corrosive organic acid ordinarily used as the solvent may reduce the reliability of the circuit board. Instead, the '931 patent speaks to a method for removing residual resin by irradiation with electromagnetic radiation.

Japanese Laid-Open Patent Publication No. 251516/93 also discloses a mounting process using a bisphenol A type epoxy resin (CV5183 or CV5183S; manufactured by Matsushita Electric Industrial Co., Ltd.). However, the removal process disclosed does not consistently permit easy removal of the

chip, the curing step is lengthy at elevated temperatures, and the process generally results in poor productivity.

Of course, mechanical methods of removing/replacing semiconductor chips from/on a substrate are known, such as by cutting the chip to be removed/replaced. See U.S. Patent No. 5,355,580 (Tsukada).

Thermoplastic underfill resins are known for use in semiconductor chip attachment. See U.S. Patent No. 5,783,867 (Belke, Jr.). However, such thermoplastic resins tend to leak under relatively modest temperature conditions. In contrast, thermosetting resins cure into a matrix, which ordinarily have greater thermal stability under end use operating temperatures.

U.S. Patent Nos. 5,512,613 (Afzali-Ardakani), 5,560,934 (Afzali-Ardakani), and 5,932,682 (Buchwalter), each refer to a reworkable thermoset composition based on a diepoxide component in which the organic linking moiety connecting the two epoxy groups of the diepoxide includes an acid cleavable acyclic acetyl group. With such acid cleavable acyclic acetyl groups forming the bases of the reworkable composition, a cured thermoset need only be introduced to an acidic environment in order to achieve softening and a loss of much of its adhesiveness.

U.S. Patent No. 5,872,158 (Kuczynski) refers to thermosetting compositions capable of curing upon exposure to actinic radiation, which are based on acetyl diacrylates, and reaction products of which are reported to be soluble in dilute acid.

U.S. Patent No. 5,760,337 (Iyer) refers to thermally reworkable crosslinked resins to fill the gap created between a semiconductor device and a substrate to which it is attached. These resins are produced by reacting a dienophile

(with a functionality greater than 1) with a 2.5-dialkyl substituted furan-containing polymer.

International Patent Publication No. PCT/US98/00858 refers to a thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected. The composition includes about 100 parts by weight of an epoxy resin, about 3 to about 60 parts by weight of a curing agent, and about 1 to about 90 parts by weight of a plasticizer. There, the area around the cured thermoset is heated at a temperature of about 190 to about 260^{0}C for a period of time ranging from about 10 seconds to about 1 minute in order to achieve softening and a loss of much of its adhesiveness.

U.S. Patent Nos. 5,948,922 (Ober) and 5,973,033 (Ober), each refer to a certain class of compounds having tertiary oxycarbonyl linkages, and compositions based on such compounds, which when cured provide thermally decomposable compositions capable of being reworked.

Notwithstanding the state-of-the-art, it would be desirable for an underfilling sealing material to provide good productivity and thermal shock resistance, while allowing the substrates with which it is to be used to be readily processed and easily separated from a semiconductor device without too extreme conditions that may compromise the integrity of the semiconductor devices remaining on the substrate or the substrate itself.

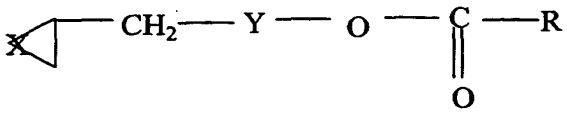
SUMMARY OF THE INVENTION

The present invention provides a thermosetting resin composition useful as an underfill sealant resin. The

composition enables a semiconductor device, such as a CSP/BGA/LGA assembly which includes a semiconductor chip mounted on a carrier substrate, to be securely connected to a circuit board by short-time heat curing and with good productivity, which demonstrates excellent heat shock properties (or thermal cycle properties), and permits the CSP/BGA/LGA assembly to be easily removed from the circuit board in the event of semiconductor device or connection failure. Similarly, a semiconductor chip may be securely connected to, and if necessary removed from, a circuit board using the inventive compositions.

The thermosetting resin composition includes a curable resin component and a curing agent. The curable resin component may be chosen from those having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one linkage selected from ether, thioether, carbonate and combinations thereof, which linkage is capable of being reworked under appropriate conditions so as to lose its adhesiveness. One such rework technique involves degrading the cured reaction product of the composition upon exposure to elevated temperature conditions and/or acidic conditions. In addition, the curable resin may be an epoxy resin, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group. Where the curable resin is not an epoxy resin, the inventive composition may include as a separate component an epoxy resin component.

The compositions may also include a monofunctional epoxy coreactant diluent represented by the following structure:



where X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents alkyl, alkenyl, aryl and the like; and R represents alkyl, alkenyl, aryl and the like, as well as an inorganic filler component. In addition, where the curing agent is not an anhydride, the inventive compositions may also include a separate anhydride component.

Reaction products of these compositions are capable of being controllably reworked through the softening and loss of their adhesiveness, such as by exposure to temperature conditions in excess of those used to cure the composition.

Although the thermosetting resin composition of the present invention is curable at a relatively low temperature in a short period of time, cured reaction products thereof have excellent heat shock properties and, moreover, can be easily split by the application of force under heated conditions. That is, semiconductor devices or semiconductor chips attached to circuit boards by cured reaction products of the thermosetting resin compositions of this invention can be easily removed by heating the reaction product, allowing it to swell with a solvent, or allowing it to swell with a solvent under heated conditions.

By using the thermosetting resin compositions of this invention, semiconductor devices, such as CSP/BGA/LGA assemblies, or semiconductor chips can be securely connected to a circuit board by short-time heat curing and with good productivity, with the resulting mounting structure demonstrating excellent heat shock properties (or thermal cycle properties). Moreover, in the event of failure, the

semiconductor device or semiconductor chip can be easily removed. This makes it possible to reuse the circuit board, thereby achieve an improvement in the yield of the production process and reducing production cost.

The benefits and advantages of the present invention will become more readily apparent after a reading the "Detailed Description of the Invention", with reference to the figures.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 depicts a cross-sectional view showing an example of a semiconductor device in which the thermosetting resin composition of the present invention is used.

FIG. 2 depicts a cross-sectional view of a semiconductor device which has been removed from the circuit board for repairing purposes.

FIG. 3 depicts a cross-sectional view showing an example of a semiconductor flip chip assembly in which the thermosetting resin composition of the present invention is used.

FIG. 4 depicts a flow diagram of a procedure useful to rework a cured thermosetting resin composition in accordance with the present invention, so as to remove a semiconductor device from a circuit board to which it had been attached.

FIG. 5 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (■) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin ( ) loses weight by virtue of thermal degradation.

FIG. 6 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (■) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin (□) loses weight by virtue of thermal degradation.

FIG. 7 depicts a temperature vs. weight loss trace of a thermal gravimetric analysis demonstrating the temperatures at which a composition in accordance with this invention (◆) loses weight by virtue of thermal degradation contrasted to the temperatures at which a composition based on bisphenol-F-type epoxy resin (◇) loses weight by virtue of thermal degradation.

FIG. 8 depicts a ^{13}C NMR spectra of "ANCAMINE" 2337S.

FIG. 9 depicts a FT-IR spectra of "ANCAMINE" 2337S.

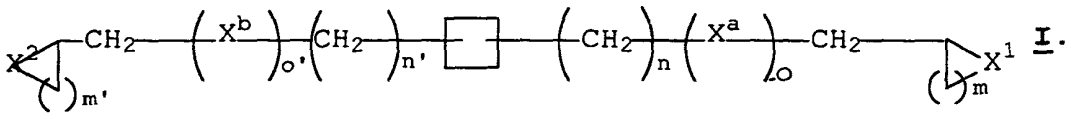
DETAILED DESCRIPTION OF THE INVENTION

The thermosetting resin composition broadly includes a curable resin component and a curing agent.

The curable resin component may be chosen from those having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one linkage selected from ether, thioether, carbonate and combinations thereof, which linkage is capable of being reworked under appropriate conditions so as to lose its adhesiveness. One such rework technique involves degrading the cured reaction product of the inventive composition upon exposure to elevated temperature conditions and/or acidic conditions. In addition, the curable resin may be an epoxy resin, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one

terminal epoxy group. Where the curable resin is not itself an epoxy resin, the inventive composition may include as a separate component an epoxy resin component.

In one aspect of the invention, the curable resin may be represented by the following structure:

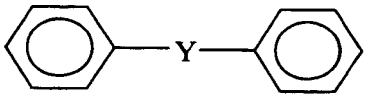


I.

The box may represent one or more structural linkages including aromatic rings(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms, examples of which are given below.

X^1, X^2 and X^a and X^b may be the same or different and represent the heteroatoms, oxygen and sulfur. The letter designations, m and m^1, represent integers within the range of 1 to 3, n and n^1 represent integers within the range of 0 to 8, and o and o^1 represent integers within the range of 1 to 3. The box of the core structure of aromatic rings within the curable resin of structure I may be individual aromatic rings, or aromatic ring systems having multiple aromatic units joined in fused ring systems, joined in bi-aryl (such as, biphenyl) or bis-aryl (such as bisphenol A or bisphenol F, or bisphenol compounds joined by a heteroatom) systems, joined in cycloaliphatic-aromatic hybrid ring systems, or joined in oligomeric (such as, novolac-type) systems, examples of which include, among others, naphthalene, anthracene, phenanthracene and fluorene.

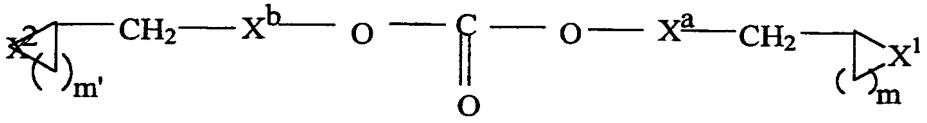
For instance, the box may represent the structural linkage



where Y may or may not be present and when present is carbon, or the heteroatom, oxygen or sulfur. Or the box may represent a phenylene group. Either of these representations may bear substitution at one or more locations on the aromatic ring(s) with functional groups ordinarily present on aromatic rings(s), such as alkyl, alkenyl, halo, nitro, carboxyl, amino, hydroxyl, thio, and the like.

For instance, particularly desirable curable resins within structure I include MPG, [bis[4(2,3-epoxy-propylthio)phenyl]-sulfide (CAS Reg. No. 84697-35-8), available commercially from Sumitomo Seika Chemicals Co., Ltd., Osaka, Japan and XBO, xylene bisoxetane (CAS Reg. No. 142627-97-2), available commercially from UBE Industries, Ltd., Tokyo, Japan.

In another aspect of the invention, the curable resin is represented by the following structure:



II.

X^1 and X^2 are as above; X^a and X^b may be the same or different, may or may not be present, and when present represent alkyl, alkenyl, aryl and the like; and the letter designations, m and m^1 are as above.

The heteroatom-containing carbocyclic structures pending from the core structure may be three, four or five membered rings with the heteroatom being an oxygen and/or sulfur atom. These ring structures cross-link with one another under appropriate conditions to form reaction products of the compositions of the present invention.

The carbonate linkage is degradable upon exposure to elevated temperature conditions, with or without the presence of acid. This linkage is capable of degrading to liberate carbon dioxide gas.

The temperature used to effect such degradation of compositions within the scope of the present invention may be as great as 50°C lower than the temperatures required to degrade ordinary epoxy-based compositions used for this purpose, such as those based on bisphenol-A-type epoxy resins or bisphenol-F-type epoxy resins, which are ordinarily in the vicinity of about 300°C or more. (See Examples section.)

A particularly desirable curable resin within structure II includes CBO, carbonate bisoxetane (CAS Reg. No. 60763-95-3), available commercially from UBE Industries, Ltd., Tokyo, Japan.

In still another aspect of the invention, the curable resin is an epoxy resin, where at least a portion of such epoxy resin includes an epoxy resin having at least one alkylene oxide residue position adjacent at least one terminal epoxy group. The epoxy resin may be based on mono- or multi-functional aliphatic epoxies, epoxies with a cycloaliphatic ring structure or system, or epoxies with an aromatic ring structure or system, and combinations thereof

For instance the epoxy resin may include any common epoxy resin, such as a multifunctional epoxy resin.

Ordinarily, the multifunctional epoxy resin should be included in an amount within the range of about 15% by weight to about 75% by weight of the total of the epoxy resin component. In the case of bisphenol-F-type epoxy resin, desirably the amount thereof should be in the range of from about 35% by weight to about 65% by weight, such as about 40% by weight to about 50% by weight of the total of the epoxy resin component.

Examples of the multifunctional epoxy resin include bisphenol-A-type epoxy resin, bisphenol-F-type epoxy resin (such as RE-404-S from Nippon Kayaku, Japan), phenol novolac-type epoxy resin, and cresol novolac-type epoxy from resin (such as "ARALDITE" ECN 1871 from Ciba Specialty Chemicals, Hawthorne, New York).

Other suitable epoxy resins include polyepoxy compounds based on aromatic amines and epichlorohydrin, such as N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether; and N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate.

Among the epoxy resins suitable for use herein also include polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradename "EPON", such as "EPON" 828, "EPON" 1001, "EPON" 1009, and "EPON" 1031 from Shell Chemical Co.; "DER" 331, "DER" 332, "DER" 334, and "DER" 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of such as "DEN" 431, "DEN" 438, and "DEN" 439 from Dow Chemical. Cresol analogs are also available commercially under the tradename "ARALDITE", such as "ARALDITE" ECN 1235, "ARALDITE" ECN 1273, and "ARALDITE" ECN 1299 from Ciba Specialty Chemicals Corporation. SU-8 is a bisphenol-A-type epoxy

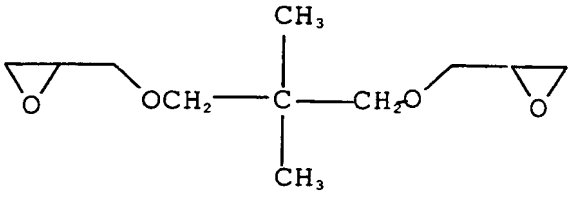
novolac available from Interez, Inc. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include GLYAMINE" 135, "GLYAMINE" 125, and "GLYAMINE" 115 from F.I.C. Corporation; "ARALDITE" MY-720, "ARALDITE" 0500, and "ARALDITE" 0510 from Ciba Specialty Chemicals and PGA-X and PGA-C from the Sherwin-Williams Co.

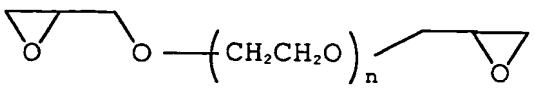
An of course combinations of the different epoxy resins are also desirable for use herein.

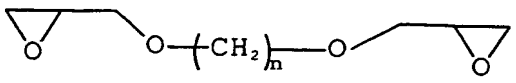
It is particularly desirable for the portion of the epoxy resin component having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group to be present in an amount of at least about 5% by weight of the total of epoxy resin component.

Examples of aliphatic epoxies with alkylene oxide residues include, but are not limited to, mono-, di- or multi-functional epoxies containing ether linkages, such as primary, secondary and tertary alkylene diol diglycidyl ethers, and epoxies containing mono- or poly-alkylene oxide residues (such as ethylene oxide, propylene oxide, butylene oxide, pentylene oxide, and hexylene oxide residues).

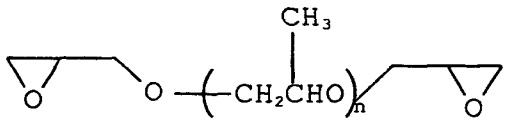
For instance,



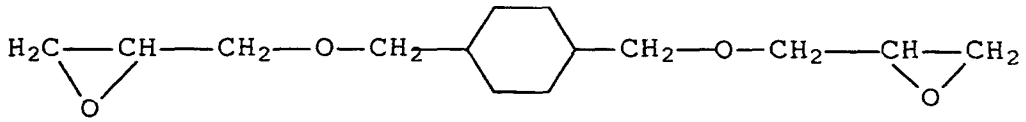




where n is an integer from 1 to about 18, are each appropriate, individually or in combination, for use as at least a portion of the epoxy resin component.

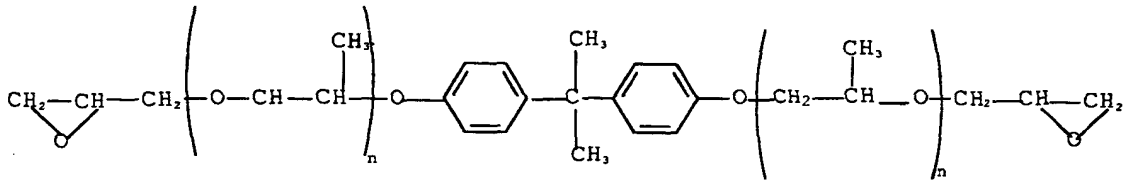


Examples of cycloaliphatic epoxies with alkylene oxide residues include mono-, di- or multi functional cyclohexyl epoxies; hydrated bisphenol A-type epoxies; and hydrated bisphenol F-type epoxies, containing alkylene ether residues. DME-100 (1,4-cyclohexane dimethanol diglycidyl ether, available commercially from New Japan Chemical Co., Ltd.) as shown below is one such example.

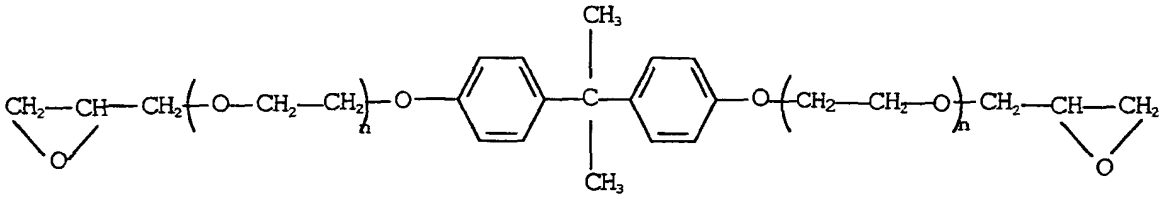


Examples of aromatic epoxies with alkylene oxide residues include mono-, di- or multi- functional epoxies such as bisphenol A type epoxies; bisphenol F type epoxies; phenol novolac type epoxies; and cresol novolac type epoxies, containing alkylene ether residues.

Examples of such epoxies include BEO-60E (ethoxylated bisphenol A di-glycidyl ether, available commercially from New Japan Chemical Co., Ltd.), and BPO-20E (propyloxylated bisphenol A di-glycidyl ether, available commercially from New Japan Chemical Co., Ltd.), which are shown below:



where n is an integer between and about 1 and 20, which for BPO-60E n is 1, and



where n is an integer between and about 1 and 20, which for BEO-60E n is 3.

The curable resin component should be present in the composition in an amount which the range of about 10% by weight to about 95% by weight, desirably about 20% by weight to about 80% by weight, such as about 60% by weight

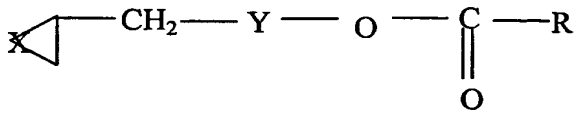
In yet another aspect of the invention, the epoxy resin is used in combination with a monofunctional epoxy coreactant diluent.

Appropriate monofunctional epoxy coreactant diluents for use herein include those that have a viscosity which is lower than that of the epoxy resin component, ordinarily, less than about 250 cps.

The monofunctional epoxy coreactant diluents should have an epoxy group with an alkyl group of about 6 to about 28 carbon atoms, examples of which include C_{6-28} alkyl glycidyl

ethers, C_{6-28} fatty acid glycidyl esters and C_{6-28} alkylphenol glycidyl ethers.

A particularly desirable coreactant diluent is represented by:



III.

where X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents an alkyl (linear, branched, cyclo or bicyclo), or alkenyl (linear, branched, cyclo or bicyclo) and the like linkage of from one to about twenty carbon atoms, linkage and an aryl (one or more aromatic ring(s) or ring system(s)) linkage of from about six to about twenty carbon atoms.

Commercially available monofunctional epoxy coreactant diluents include those from Pacific Epoxy Polymers, Richmond, Michigan, under the trade designations PEP-6770 (glycidyl ester of neodecandoic acid), PEP-6740 (phenyl glycidyl ether) and PEP-6741 (butyl glycidyl ether).

In the event such a monofunctional epoxy coreactant diluents is included, such coreactant diluent should be employed in an amount of up to about 5% by weight to about 15% by weight, such as about 8% by weight to about 12% by weight, based on the total weight of the composition.

As the curing agent, a variety of materials may be chosen including amine compounds, amide compounds, imidazole compounds, modified amine compounds and modified imidazole compounds (modified compound are also called derivatives thereof).

Examples of the amine compounds include aliphatic polyamines, such as diethylenetriamine, triethylenetetramine and diethylaminopropylamine; aromatic polyamines, such as m-

xylenediamine and diaminodiphenylamine; and alicyclic polyamines, such as isophoronediamine and menthenediamine.

Of course, combinations of these amine compounds are also desirable for use in the compositions of the present invention.

Examples of the amide compounds include cyano-functionalized amides, such as dicyandiamide.

Examples of the imidazole compounds include imidazole, isoimidazole, and substituted imidazoles -- such as alkyl-substituted imidazoles (e.g., 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole and addition products of an imidazole and trimellitic acid, 2-n-heptadecyl-4-methylimidazole and the like, generally where each alkyl substituent contains up to about 17 carbon atoms and desirably up to about 6 carbon atoms), and aryl-substituted imidazoles [e.g., phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, 2-(2-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-napthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-

methoxystyrylimidazole, and the like, generally where each aryl substituent contains up to about 10 carbon atoms and desirably up to about 8 carbon atoms].

Examples of commercial imidazole compounds are available from Air Products, Allentown, Pennsylvania under the trade designation "CUREZOL" 1B2MZ and from Synthron, Inc., Morganton, North Carolina under the trade designation "ACTIRON" NXJ-60.

Of course, combinations of these imidazole compounds are also desirable for use in the compositions of the present invention.

Examples of the modified amine compounds include epoxy amine additives formed by the addition of an amine compound to an epoxy compound, and examples of the modified imidazole compounds include imidazole adducts formed by the addition of an imidazole compound to an epoxy compound.

A commercially available modified amine compound particularly useful herein is "NOVACURE" HX-3722 (an imidazole/bisphenol A epoxy adduct dispersed in bisphenol A epoxy resin, commercially available from Asahi-Ciba Ltd.), and "MY-24" (an imidazole/bisphenol A epoxy adduct, commercially available from Ajinomoto Co., Ltd.).

Another such modified amine compound particularly useful herein is available commercially from Air Products and Chemicals, Inc., Allentown, Pennsylvania under the "ANCAMINE" 2337S tradename. "ANCAMINE" 2337S is described by Air Products as a modified aliphatic amine, which is a light yellow powder in appearance with a particle size of 90% $\leq$ 10 μ, whose melting point is in the range of 145-172^{0}F. "ANCAMINE" 2337S is reported to have an amine value of 260 (mg KOH/gram), and rapid reactivity above a temperature of 158^{0}F. It is believed that "ANCAMINE" 2337S is a novolac-type resin

that has been modified through reaction with aliphatic amines, such as polyamines, pyrazines, pyridines, pyroles and pyrazoles. (See FIGs. 8-9 for characterizing data.) The "ANCAMINE" 2337S itself is substantially insoluble at room temperature in conventional non-basic organic solvents, though was found to be soluble in pyridine.

The curing agent should be present in an amount with the range of about 5% by weight to about 90% by weight, desirably about 20% by weight to about 60% by weight, such as about 50% by weight of the total composition.

The compositions may also include an anhydride component where the curing agent of the compositions is not based on anhydride reactivity, as well as an inorganic filler component.

Appropriate anhydride compounds for use herein include mono- and poly-anhydrides, such as hexahydrophthalic anhydride ("HHPA") and methyl hexahydrophthalic anhydride ("MHHPA") (commercially available from Lindau Chemicals, Inc., Columbia, South Carolina, used individually or as a combination, which combination is available under the trade designation "LINDRIDE" 62C) and 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (commercially available from ChrisKev Co., Leewood, Kansas under the trade designation B-4400). In addition, "MTA-15" (mixture of glycol tris-anhydrotrimeritate and MHHPA, commercially available from New Japan Chemical Co., Ltd.) and "MH-700" (MHHPA, commercially available from New Japan Chemical Co., Ltd.) are particularly desirable choices.

Of course, combinations of these anhydride compounds are also desirable for use in the compositions of the present invention. When used, the anhydride compound may be present in an amount within the range of about 5% by weight to about

90% by weight, desirably about 10% by weight to about 60% by weight, such as about 40% by weight of the total composition.

As an inorganic filler component, many materials are potentially useful. For instance, the inorganic filler component may often include reinforcing silicas, such as fused silicas, and may be untreated or treated so as to alter the chemical nature of their surface. Virtually any reinforcing fused silica may be used.

Particularly desirable ones have a low ion concentration and are relatively small in particle size (e.g., in the range of about 2-10 microns, such as on the order of about 2 microns), such as the silica commercially available from Admatechs, Japan under the trade designation SO-E5.

Other desirable materials for use as the inorganic filler component include those constructed of or containing aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride and combinations thereof. When used, the inorganic filler component may be present in an amount within the range of about 5% by weight to about 95% by weight, desirably about 20% by weight to about 60% by weight, such as about 40% by weight of the total composition.

In addition, the composition may also include a flowability agent, such as a silane and/or titanate.

Appropriate silanes for use herein include octyl trimethoxy silane (commercially available from OSI Specialties Co., Danbury, Connecticut under the trade designation A-137), and methacryloxy propyl trimethoxy silane (commercially available from OSI under the trade designation A-174).

Appropriate titanates for use herein include titanium IV tetrakis [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0] [bis(ditridecylphosphito-0), dihydrogen]$_2$

(commercially available from Kenrich Petrochemical Inc., Bayonne, New Jersey under the trade designation KR-55).

When used, the flowability agent may be used in an amount of 0 to about 2 parts by weight, per 100 parts of the epoxy resin.

In addition, adhesion promoters, such as the silanes, glycidyl trimethoxysilane (commercially available from OSI under the trade designation A-187) or gamma-amino propyl triethoxysilane (commercially available from OSI under the trade designation A-1100), may be used.

Cyanate esters may also be used in the inventive compositions. The cyanate esters useful as a component in the inventive compositions may be chosen from dicyanatobenzenes, tricyanatobenzenes, dicyanatonaphthalenes, tricyanatonaphthalenes, dicyanato-biphenyl, bis(cyanatophenyl)methanes and alkyl derivatives thereof, bis(dihalocyanatophenyl)propanes, bis(cyanatophenyl)ethers, bis(cyanatophenyl)sulfides, bis(cyanatophenyl)propanes, tris(cyanatophenyl)phosphites, tris(cyanatophenyl)phosphates, bis(halocyanatophenyl)methanes, cyanated novolac, bis[cyanatophenyl(methylethylidene)]benzene, cyanated bisphenol-terminated thermoplastic oligomers, and combinations thereof.

More specifically, aryl compounds having at least one cyanate ester group on each molecule and may be generally represented by the formula $Ar(OCN)_m$, where Ar is an aromatic radical and m is an integer from 2 to 5. The aromatic radical Ar should contain at least 6 carbon atoms, and may be derived, for example, from aromatic hydrocarbons, such as benzene, biphenyl, naphthalene, anthracene, pyrene or the like. The aromatic radical Ar may also be derived from a polynuclear aromatic hydrocarbon in which at least two aromatic rings are

attached to each other through a bridging group. Also included are aromatic radicals derived from novolac-type phenolic resins -- i.e., cyanate esters of these phenolic resins. The aromatic radical Ar may also contain further ring-attached, non-reactive substituents.

Examples of such cyanate esters include, for instance, 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane; tris(4-cyanatophenyl)-phosphite; tris(4-cyanatophenyl)phosphate; bis(3-chloro-4-cyanatophenyl)methane; cyanated novolac; 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and cyanated bisphenol-terminated polycarbonate or other thermoplastic oligomer.

Other cyanate esters include cyanates disclosed in U.S. Patent Nos. 4,477,629 and 4,528,366, the disclosure of each of which is hereby expressly incorporated herein by reference; the cyanate esters disclosed in U.K. Pat. No. 1,305,702, and the cyanate esters disclosed in International Patent Publication WO 85/02184, the disclosure of each of which is hereby expressly incorporated herein by reference. Of course, combinations of these cyanate esters within the imidazole component of the compositions of the present invention are also desirably employed herein.

A particularly desirable cyanate ester for use herein is available commercially from Ciba Specialty

Chemicals, Tarrytown, New York under the tradename "AROCY" L10 [1,1-di(4-cyanatophenylethane)].

When used, the cyanate esters may be used in an amount of about 1 to about 20% by weight based on the total amount of the epoxy resin component.

Conventional additives may also be used in the compositions of the present invention to achieve certain desired physical properties of the composition, the cured reaction product, or both.

For instance, it may be desirable in certain instances (particularly where a large volume of inorganic filler component is used) to include a multifunctional epoxy resin reactive diluent, examples of which include those from Pacific Epoxy Polymers, under the trade designations PEP-6752 (trimethylolpropane triglycidyl ether) and PEP-6760 (diglycidyl aniline).

The thermosetting resin composition of the present invention may further contain other additives, such as defoaming agents, leveling agents, dyes and pigments. Moreover, photopolymerization initiators may also be incorporated therein, provided that such initiators do not adversely affect the properties of the composition or reaction products formed therefrom.

The thermosetting resin composition of the present invention may be formulated as a one-part composition, in which all the ingredients are mixed together, or as a two-part composition, in which the epoxy resin and the curing agent are stored separately and mixed thereafter prior to use. Accordingly, the curing agent used in the present invention can generally be any of the curing agents that are used in one-part and two-part epoxy resin formulations, particularly those noted above.

The thermosetting resin compositions according to the present invention are capable of penetrating into the space between the circuit board and the semiconductor device. These inventive compositions also demonstrate a reduced viscosity, at least under elevated temperature conditions, and thus are capable of penetrating into that space. It is desirable to prepare the thermosetting resin composition by selecting the types and proportions of various ingredients to reach a viscosity at 25°C of 10,000 mPa·s or less, such as 3,000 - 4,000 mPa·s, so as to improve its ability to penetrate into the space (e.g., of 50 to 500μm) between the circuit board and the semiconductor device.

Reference to FIG. 1 shows an example of a semiconductor device mounting structure, such as a CSP, in which the thermosetting resin composition of the present invention is used.

The semiconductor device 4 is one formed by connecting a semiconductor chip (so-called bare chip) 2, such as LSI, to a carrier substrate 1 and sealing the space therebetween suitably with resin 3. This semiconductor device is mounted at a predetermined position of the circuit board 5, and electrodes 8 and 9 are electrically connected by a suitable connection means such as solder. In order to improve reliability, the space between carrier substrate 1 and circuit board 5 is sealed with the cured product 10 of a thermosetting resin composition. The cured product 10 of the thermosetting resin composition need not completely fill the space between carrier substrate 1 and circuit board 5, but may fill it to such an extent as to relieve stresses caused by thermal cycling.

Carrier substrates may be constructed from ceramic substrates made of Al_2O_3, SiN_3 and mullite (Al_2O_3-SiO_2); substrates or tapes made of heat-resistant resins such as polyimides; glass-reinforced epoxy, ABS and phenolic substrates which are also used commonly as circuit boards; and the like.

As regards flip chip assemblies, reference to FIG. 3 shows a flip chip assembly in which a semiconductor chip has been mounted onto a circuit board, and the underfilling sealed with a thermosetting resin composition of the present invention.

The flip chip assembly 34 is formed by connecting a semiconductor chip (a bare chip) 32 to a circuit board 31 and sealing the space therebetween suitably with a thermosetting resin composition 33. This semiconductor device is mounted at a predetermined position on the circuit board 31 and electrodes 35 and 36 are electrically connected by a suitable electrical connection means 37 and 38, such as solder. In order to improve reliability, the space between the semiconductor chip 32 and the circuit board 31 is sealed with a thermosetting resin composition 33 and then cured. The cured product of the thermosetting resin composition should completely fill that space.

No particular limitation is placed on the means for electrically connecting the semiconductor chip to the carrier substrate, and there may be employed connection by a high-melting solder or electrically (or anisotropically) conductive adhesive, wire bonding, and the like. In order to facilitate connections, the electrodes may be formed as bumps. Moreover, in order to improve the reliability and durability of connections, the space between the semiconductor chip and the

carrier substrate may be sealed with a suitable resin. The semiconductor devices that can be used in the present invention include CSPs, BGAs, and LGAs.

No particular limitation is placed on the type of circuit board used in the present invention, and there may be used any of various common circuit boards such as glass-reinforced epoxy, ABS and phenolic boards.

Next, the mounting process is described below. Initially, cream solder is printed at the necessary positions of a circuit board and suitably dried to expel the solvent. Then, a semiconductor device is mounted in conformity with the pattern on the circuit board. This circuit board is passed through a reflowing furnace to melt the solder and thereby solder the semiconductor device. The electrical connection between the semiconductor device and the circuit board is not limited to the use of cream solder, but may be made by use of solder balls. Alternatively, this connection may also be made through an electrically conductive adhesive or an anisotropically conductive adhesive. Moreover, cream solder or the like may be applied or formed on either the circuit board or the semiconductor device. In order to facilitate subsequent repairs, the solder, electrically or anisotropically conductive adhesive used should be chosen bearing in mind its melting point, bond strength and the like.

After the semiconductor device is electrically connected to the circuit board in this manner, the resulting structure should ordinarily be subjected to a continuity test or the like. After passing such test, the semiconductor device may be fixed thereto with a resin composition. In this way, in the event of a failure, it is easier to remove the semiconductor device before fixing it with the resin composition.

Then, using a suitable application means such as dispenser, a thermosetting resin composition is applied to the periphery of the semiconductor device. When this composition is applied to the semiconductor device, it penetrates into the space between the circuit board and the carrier substrate of the semiconductor device by capillary action.

Next, the thermosetting resin composition is cured by the application of heat. During the early stage of this heating, the thermosetting resin composition shows a significant reduction in viscosity and hence an increase in fluidity, so that it more easily penetrates into the space between the circuit board and the semiconductor device. Moreover, by providing the circuit board with suitable venting holes, the thermosetting resin composition is allowed to penetrate fully into the entire space between the circuit board and the semiconductor device.

The amount of thermosetting resin composition applied should be suitably adjusted so as to fill the space between the circuit board and the semiconductor device almost completely.

When the above-described thermosetting resin composition is used, it is usually cured by heating at a temperature of about 80°C to about 150°C for a period of time of about 5 to about 60 minutes. Thus, the present invention can employ relatively low-temperature and short-time curing conditions and hence achieve very good productivity. The semiconductor device mounting structure illustrated in FIG. 1 is completed in this manner.

In the mounting process using the thermosetting resin composition of the present invention, after the semiconductor device is mounted on the circuit board as described above, the resulting structure is tested with

respect to characteristics of the semiconductor device, connection between the semiconductor device and the circuit board, other electrical characteristics, and the state of sealing. In the event a failure is found, repair can be made in the following manner.

The area around the semiconductor device that has failed is heated at a temperature of about 190°C to about 260°C for a period of time ranging from about 10 seconds to about 60 seconds. Although no particular limitation is placed on the heating means, local heating is preferred. There may be employed a relatively simple means such as the application of hot air to the failure site.

As soon as the solder is melted and the resin is softened to cause a reduction in bond strength, the semiconductor device is pulled apart.

After the semiconductor device 4 is removed as shown in FIG. 2, a residue 12 of the cured reaction product of the thermosetting resin composition and a residue 14 of the solder are left on the circuit board 5. The residue of the cured product of the thermosetting resin composition can be removed, for example, by scraping it off after the residue has been softened by heating it to a predetermined temperature, allowing it to swell with solvent, or allowing it to swell with solvent while heating it to a predetermined temperature.

The residue can be most easily removed by using both heating and solvent. For example, the residue can be scraped off after it has been softened by allowing the residual resin to swell with solvent while keeping the entire circuit board at a temperature of about 100°C (usually in the range of about 80°C to about 120°C).

The solvent used for this purpose is one which causes cured reaction products of the thermosetting resin

composition to swell, thereby reducing bond strength to such an extent that the cured material can be scraped off from the circuit board. Useful solvents include organic ones, for example, alkyl chlorides, such as methylene chloride; glycol ethers, such as ethyl cellulose and butyl cellulose; diesters of dibasic acids, such as diethyl succinate; and N-methylpyrrolidone. Of course, appropriate combinations may also be employed.

Where a circuit-protecting resist has already been connected to the circuit board, the chosen solvents should cause no damage to the resist. Desirable solvents with this in mind include glycol ethers and N-methylpyrrolidone.

The residue of the solder can be removed, for example, by use of a solder-absorbing braided wire.

Finally, on the circuit board which has been cleaned according to the above-described procedure, a new semiconductor device may be mounted again in the same manner as described previously. Thus, the repair of the failure site is completed.

Where a failure is found in the circuit board, the semiconductor device can be reused by removing the residue 13 of the cured reaction product of the thermosetting resin composition and the residue 15 of the solder left on the bottom of the semiconductor device in the same manner as described above. (See FIG. 4.)

The invention will be further illustrated by the following non-limiting examples.

EXAMPLES

Example 1

Thermosetting Resin Composition

A thermosetting resin compositions in accordance with the present invention may be prepared from the components as noted below in Tables 1a-1f.

Table 1a

Component		Sample No./Amt (grams)							
Type	Identity	1	2	3	4	5	6	7	8
Epoxy	BEO - 60E	61.176	42.824	36.706	--	--	--	--	--
	BPO - 20E	--	--	--	65.488	58.939	45.842	32.744	59.002
	DME - 100	--	--	--	--	--	--	--	--
Curing Agent	NOVACURE HX-3722	6.275	4.392	3.765.	--	--	--	--	6.254
Anhydride	MTA - 15	32.549	22.784	19.529	--	--	--	--	34.744
	MH - 700	--	--	--	32.417	29.175	22.692	16.208	--
Inorganic Filler	SO - E5	--	30	40	--	10	30	50	--

Table 1b

Component		Sample No./Amt (grams)							
Type	Identity	9	10	11	12	13	14	15	16
Epoxy	BEO - 60E	--	--	--	--	--	--	--	--
	BPO - 20E	41.301	35.402	--	--	--	--	--	--
	DME - 100	--	--	48.426	44.262	44.550	40.095	35.640	31.185
Curing Agent	NOVACURE HX-3722	4.378	3.752	--	6.246	5.750	5.175	4.600	4.025
	MY-24	--	--	2.082	--	--	--	--	--
Anhydride	MTA - 15	24.321	20.846	--	--	--	--	--	--
	MH - 700	--	--	49.492	49.492	48.700	43.830	38.960	34.090
Inorganic Filler	SO - E5	--	30	40	--	10	30	50	--

Table 1c

Component		Sample No./Amt. (grams)						
Type	Identity	17	18	19	20	21	22	23
Resin	MPG	47.80	45	54.05	48.65	43.24	--	--
	XBO	--	--	--	--	--	45.80	98
Curing Agent	NOVACURE HX-3722	6	55	2.7	2.43	2.16	6	--
	MH - 700 (Anhydride)	46.20	--	43.25	38.92	34.60	48.20	--
	SI 100 (Cationic Catalyst)	--	--	--	--	--	--	2
Inorganic Filler	SO-E5	--	--	--	10	20	--	--

For comparative purposes, Sample Nos. 24-30 were prepared substantially as Sample Nos. 17-23, save for the curable resin, which was replaced with a comparable amount of an epoxy resin -- either bisphenol-A-type epoxy resin or bisphenol-F-type epoxy resin. See Table 1d.

Table 1d

Component		Sample No./Amt. (grams)						
Type	Identity	24	25	26	27	28	29	30
Epoxy	Bisphenol A	45	48.42	43.58	38.74	--	--	--
	Bisphenol F	--	--	--	--	45	45.80	98
Curing Agent	NOVACURE HX-3722	55	6.32	5.68	5.05	55	6	--
	MH - 700 (Anhydride)	--	45.26	40.74	36.21	--	48.20	--
	SI 100 (Cationic Catalyst)	--	--	--	--	--	--	2
Inorganic Filler	SO-E5	--	--	10	20	--	--	--

Table 1e

Component		Sample No./Amt. (grams)								
Type	Identity	31	32	33	34	35	36	37	38	39
Resin	CBO	40	98	85.75	78.40	61.25	49	36.75	19.60	12.25
	RE403S	–	–	12.25	19.60	36.75	49	61.25	76.40	85.75
Curing Agent	NOVACURE HX-3722	6	–	–	–	–	–	–	–	–
	MH-700 (Anhydride)	54	–	–	–	–	–	–	–	–
	SI 100 (Cationic Catalyst)	–	2	2	2	2	2	2	2	2
Inorganic Filler	SO-E5	–	–	–	–	–	–	–	–	–

For comparative purposes, Sample Nos. 40-48 were prepared as Sample Nos. 31-39, save for the curable resin, which was replaced with a comparable amount of an epoxy resin -- either bisphenol-A-type epoxy resin or bisphenol-F-type epoxy resin. The comparative samples are presented in Table 1f.

Table 1f

Component		Sample No./Amt. (grams)								
Type	Identity	40	41	42	43	44	45	46	47	48
Epoxy	Bisphenol A	–	45	48.42	43.58	38.74	–	–	–	–
	Bisphenol F	98	–	–	–	–	45	46	41.40	36.80
Curing Agent	NOVACURE HX-3722	–	55	6.32	5.68	5.05	55	6	5.40	4.80
	MH-700 (Anhydride)	–	–	45.26	40.74	36.21	–	48	10	20
	SI 100 (Cationic Catalyst)	2	–	–	–	–	–	–	–	–
Inorganic Filler	SO-E5	–	–	–	10	20	–	–	10	20

Table 1g

Component		Sample No./Amt (grams)		
Type	Identity	49 (range)	50	51
Epoxy	Bisphenol A	–	–	51.4
	Bisphenol F	48.83 - 53.97	51.4	–
Curing Agent	ANCAMINE 2337S	34.49 - 38.12	36.3	36.3
Coreactant	Glycidyl neodecanoate	11.69 - 12.92	12.3	12.3

Physical Properties

In the uncured state, the compositions were observed to have the viscosity values in mPa·s as set forth in Table 2.

In the cured state, reaction products of the composition were observed to have a glass transition temperature ("Tg") as measured by thermal mechanical analysis ("TMA"), α_1 and α_2, and expansion when cycled between extreme temperatures of about 0°C and about 140°C as set forth in Tables 2a-2d.

Table 2a

Sample No.	Physical Properties				
	Visc. (mPa·s)	Tg (°C)	α_1	α_2	Expansion (mm)
1	1838	50.50	69.34	179.96	0.190
2	4534	50.12	53.20	150.14	0.160
3	8671				
4	1047	66.25	64.28	188.36	0.180
5	1342	69.24	59.66	179.84	0.175
6	2521	67.36	49.26	159.2	0.175
7	13450	68.4	36.3	136.7	0.150
8	5303	84.86	60.16	180.00	0.160
9	12110	--	--	--	--
10	21960	--	--	--	--
11	70	--	--	--	--
12	63	90.82	65.84	175.92	0.165
13	75	83.17	65.40	180.28	0.160
14	95	87.14	59.71	174.56	0.160
15	133	84.33	56.00	159.20	0.135
16	167	87.61	49.12	147.07	0.135

Table 2b

Sample No.	Physical Properties				
	Visc. (mPas)	Tg (°C)	α_1	α_2	Adhesion Strength (N/mm^2)
17	--	--	--	--	--
18	3108	66.40	57.78	182.37	21.30
19	147.9	107.57	58.92	170.23	3.71
20	191.2	108.34	51.78	164.45	3.13
21	259.9	111.19	48.04	152.56	2.94
22	152.2	--	--	--	--
23	--	--	--	--	--
24	33490	121.61	57.12	196.61	22.61
25	815.6	132.31	59.62	182.99	4.42
26	2155	148.2	52.63	167.86	4.29
27	2585	140.86	54.79	156.27	3.57
28	334.5	119.12	58.57	172.14	5.51
29	752.9	126.89	52.83	156.27	4.77
30	315.6	127.35	49.59	163.54	--

Table 2c

Sample No.	Physical Properties				
	Visc. (mPa.s)	Tg (°C)	α_1	α_2	Adhesion Strength (N/mm^2)
31	12.20	--	--	--	--
32	43.68	-0.91	64.31	175.63	--
33	--	--	--	--	--
34	78.06	22.91	66.62	184.26	--
35	--	--	--	--	--
36	132.50	40.42	69.21	183.22	--
37	--	--	--	--	--
38	146.1	31.12	54.37	185.54	--
39	--	--	--	--	--
40	315.6	127.35	49.59	163.54	--
41	33490	121.61	57.12	196.61	22.61
42	815.6	132.31	59.62	182.99	4.42
43	2155	148.2	54.79	161.96	4.29
44	2585	140.86	52.63	156.27	3.57
45	334.5	119.12	58.57	172.14	5.51
46	15420	120.11	55.49	182.84	20.94
47	752.9	126.87	52.83	167.86	4.77
48	892.4	129.62	48.5	157.82	4.27

5

Table 2d

Sample No.	Physical Properties				
	Visc. (mPas)	Tg (°C)	α_1	α_2	Modulus (N/mm^2)
50	4000	41	60	195	5400
51	8000	--	--	--	--

The viscosity of the majority of these samples is suitable for use as an underfill sealant. That is, a viscosity less than about 10,000 mPa·s. The Tg values for the samples listed are suitable for use as an underfill sealant. Though not given in any of Tables 2a-2d, the coefficient of thermal expansion values for the samples were between about 0°C and about 140°C, which is suitable for use as an underfill sealant.

Mounting Process

Using cream solder (PS10R-350A-F92C; manufactured by Harima Chemicals, Inc.), a CSP having a package of 10mm square, an electrode diameter of 0.5mm, an electrode pitch of 1.0mm, and a carrier substrate made of alumina was mounted on a 1.6mm thick glass-reinforced epoxy board having a circuit formed thereon.

Thereafter, the thermosetting resin composition was applied to the periphery of the CSP by means of a dispenser, and then cured by heating in an environment where the temperature was held at about at 150°C for a period of time of about 60 minutes. The thermosetting resin composition penetrated into the space between the semiconductor device and the circuit board before curing completely.

Heat Shock Test

Four replicates of Sample Nos. 2 and 8 prepared as described above were exposed to a heat shock test while maintaining the replicates at a temperature of about -40°C for a period of time of about 10 minutes and thereafter an elevation of temperature to about +125°C for a period of time of about 10 minutes. After a predetermined number of thermal cycles were reached, the replicates were subjected to a continuity test to confirm the electrical connection between the CSP and the circuit board. The replicates were regarded as acceptable when continuity was confirmed to be at least 800 cycles, and unacceptable when continuity was lost owing to broken lines or the like before this number of cycles was reached. As to the mounting structure of this example, all of the replicates were acceptable even at more than 900 cycles.

Repair

Using a hot air generator, the area around the CSP fixed to the circuit board with the thermosetting resin composition as described above was heated by applying hot air at 250°C for 1 minute. Then, the CSP could be easily removed by inserting a metal piece between the CSP and the glass-reinforced epoxy board, and lifting the CSP.

While the glass-reinforced epoxy board was kept at a temperature of about 100°C by placing it on a hot plate (or by heating it with a far-infrared heater or the like), the resin left on the glass-reinforced epoxy board was allowed to swell with a solvent such as PS-1 (manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) or 7360 (manufactured by Loctite Corporation), and then scraped off with a spatula. The solder left on the glass-reinforced epoxy board was removed by use of a solder-absorbing braided wire. Residual trace resin

remaining on the glass-reinforced epoxy board was removed with acetone absorbed onto a cloth. The time required for this repairing operation was within about 3 minutes, which was sufficiently short from a practical point of view.

The ease of repair and reworkability of the cured adhesive is expressed below in Tables 3a-3d on a relative scale between 1 and 5, with 1 being an unreworkable cured adhesive and therefore incapable of repair and 5 being a reworkable cured adhesive and therefore easily repairable using the procedure described.

Table 3a

Sample No.	Reworkability	
	Heat	Acetone
1	4	3
2	3	3
3	2	--
4	4	4
5	4	3
6	3	3
7	3	3
8	4	3
9	2	--
10	2	--
11	5	--
12	5	--
13	4	3
14	4	4
15	3	3
16	3	3

Table 3b

Sample No.	Repairability/ Heat
17	--
18	3.5
19	3
20	2
21	2
22	--
23	--
24	1
25	2
26	1
27	1
28	2
29	1
30	2

Reference to FIG. 5 shows the temperature range at which a cured reaction product of a XBO-based composition curable through a cationic cure mechanism (Sample No. 23) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin curable through a cationic cure mechanism (Sample No. 30).

Reference to FIG. 6 shows the temperature range at which a cured reaction product of a MPG-based composition (Sample No. 17) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin (Sample No. 29).

Table 3c

Sample No.	Repairability/ Heat
31	--
32	5
33	--
34	4
35	--
36	3.5
37	--
38	3.5
39	--
40	2
41	1
42	2
43	1
44	1
45	1
46	2
47	1
48	1

Reference to FIG. 7 shows the temperature range at which a cured reaction product of a CBO-based composition curable through a cationic cure mechanism (Sample No. 32) in accordance with the invention loses weight by virtue of thermal degradation as it is exposed to an increase in temperature contrasted to a cured reaction product of a composition based on bisphenol-F-type epoxy resin curable through a cationic cure mechanism (Sample No. 40).

Table 3d

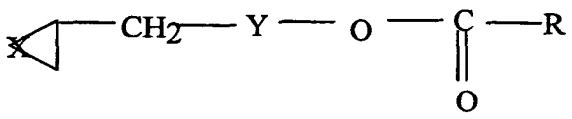
Sample No.	Repairability/ Heat
50	3.5
51	3

The full scope of the invention is measured by the claims.

What Is Claimed Is:

1. A thermosetting resin composition, reaction products of which are controllably degradable, said composition comprising:

(a) a curable resin component selected from the group consisting of curable resins having at least two heteroatom-containing carbocyclic structures pending from a core structure, with the core structure containing at least one ether, thioether or carbonate linkage that is capable of degrading upon exposure to elevated temperature conditions and/or acidic conditions, epoxy resins, at least a portion of which having at least one alkylene oxide residue positioned adjacent at least one terminal epoxy group and the combination of an epoxy resin and a coreactant diluent represented by the structure:



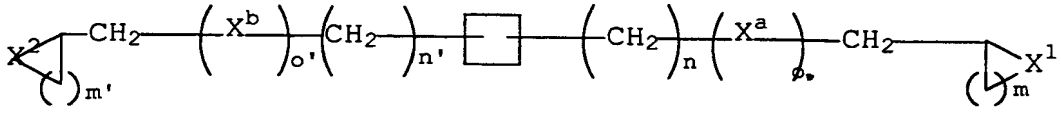
wherein X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents alkyl, alkenyl, and aryl; and R represents alkyl, alkenyl, and aryl; and

(b) a curing agent component.

2. The composition of Claim 1, further comprising an anhydride component.

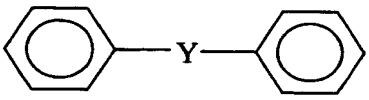
3. The composition of Claim 1, further comprising an inorganic filler component.

4. The composition of Claim 1, wherein the curable resin component is represented by the following structure:



wherein the box represents one or more aromatic ring(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms; X^1, X^2 X^a, and X^b may be the same or different and represent oxygen and sulfur; m and m^1 represent integers within the range of 1 to 3; n and n^1 represent integers within the range of 0 to 8; and o and o^1 represent integers within the range of 1 to 3.

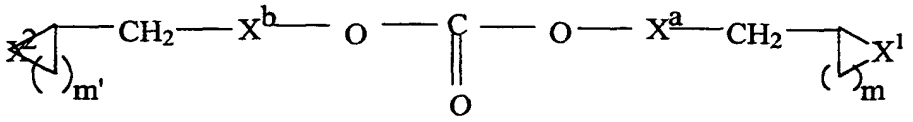
5. The composition of Claim 4, wherein the box is represented by



wherein Y may or may not be present, and where present a member selected from the group consisting of carbon, oxygen, sulfur, and phenylene.

6. The composition of Claim 4, wherein the box represents a structural linkage selected from the group consisting of individual aromatic rings, oligomeric systems and aromatic ring systems having multiple aromatic units joined in fused ring systems, joined in bi-aryl ring systems, bis-aryl ring systems, or cycloalaphatic-aromatic hybrid ring systems.

7. The composition of Claim 1, wherein the curable resin component is represented by the following structure:

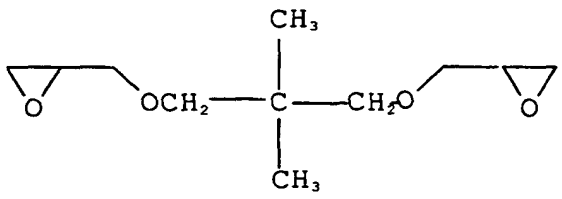


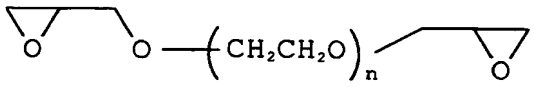
wherein X^1 and X^2 may be the same or different and represent oxygen and sulfur; X^a and X^b may be the same or different, may or may not be present, and represent alkyl, alkenyl, and aryl of one to about twenty carbon atoms, or one or more aromatic ring(s) or ring system(s), with or without interruption or substitution by one or more heteroatoms; and m and m^1 represent integers within the range of 1 to 3.

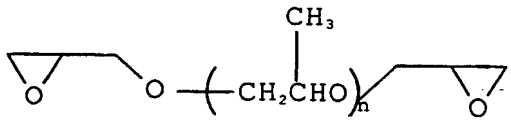
8. The composition of Claim 1, wherein the curable resin component is a member selected from the group consisting of MPG [bis[4-(2,3-epoxy-propylthio)phenyl]-sulfide], XBO [xylene bisoxetane], CBO (carbonate bisoxetane), and combinations thereof.

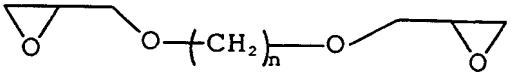
9. The composition of Claim 1, wherein the epoxy resin component includes mono- or multi-functional aliphatic epoxies, epoxies with a cycloaliphatic ring structure or system, or epoxies with an aromatic ring structure or system, and combinations thereof.

10. The composition of Claim 1, wherein the epoxy resin component includes

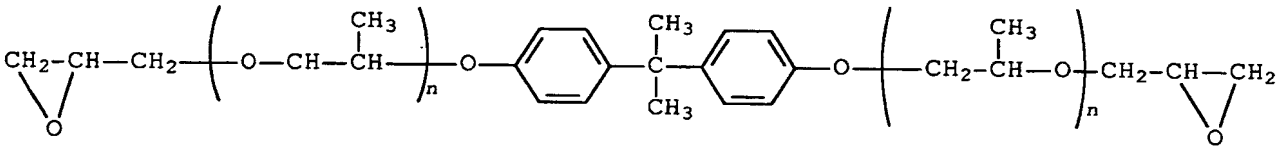


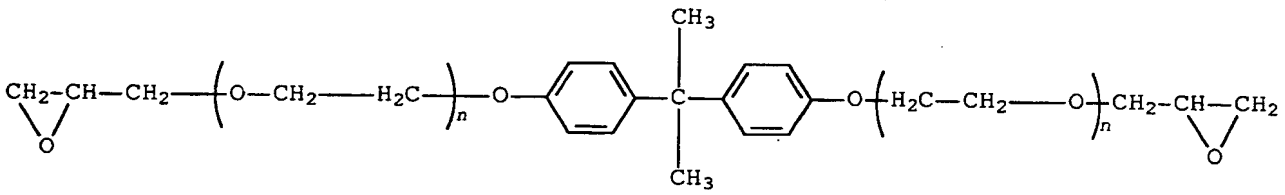




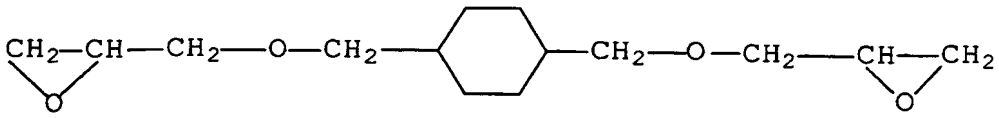


wherein n is an integer from 1 to about 18,



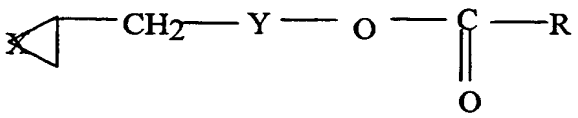


wherein n is as defined above,



and combinations thereof.

11. The composition of Claim 1, wherein the coreactant diluent is represented by the structure:



wherein X represents the heteroatoms, oxygen or sulfur; Y may or may not be present, and when present represents a linkage selected from the group consisting of linear, branched, cyclo or bicyclo alkyl or alkenyl of from one or two, respectively, to about twenty carbon atoms, and aryl of one or more aromatic ring(s) or ring system(s) of from about six to about twenty carbon atoms.

12. The composition of Claim 1, wherein the coreactant diluent is glycidyl neodecanoate.

13. The composition of Claim 1, wherein the curing agent component is a member selected from the group consisting of amine compounds, amide compounds, imidazole compounds, and derivatives and combinations thereof.

14. The composition of Claim 13, wherein the amine compounds are selected from the group consisting of aliphatic polyamines, aromatic polyamines, alicyclic polyamines and combinations thereof.

15. The composition of Claim 13, wherein the amine compounds are selected from the group consisting of diethylenetriamine, triethylenetetramine, diethylaminopropylamine, xylenediamine, diaminodiphenylamine, isophoronediamine, menthenediamine and combinations thereof.

16. The composition of Claim 13, wherein the amide compounds include cyano-functionalized amides.

17. The composition of Claim 13, wherein the imidazole compounds are selected from imidazole, isoimidazole, alkyl-substituted imidazoles, and combinations thereof.

18. The composition of Claim 13, wherein the imidazole compounds are selected from 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, 2-butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole and addition products of an imidazole and trimellitic acid, 2-n-heptadecyl-4-methylimidazole, aryl-substituted imidazoles, phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-naphthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-methoxystyrylimidazole, and combinations thereof.

19. The composition of Claim 13, wherein the modified amine compounds include epoxy amine additives formed by the addition of an amine compound to an epoxy compound.

20. The composition of Claim 13, wherein the modified amine compounds include "ANCAMINE" 2337S.

21. The composition of Claim 13, wherein the modified amine compounds are novolac-type resin modified through reaction with aliphatic amines.

22. The composition of Claim 13, wherein the modified imidazole compounds include imidazole adducts formed by the addition of an imidazole compound to an epoxy compound.

23. The composition of Claim 2, wherein the anhydride component is a member selected from the group consisting of hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, and combinations thereof.

24. The composition of Claim 3, wherein the inorganic filler component is a member selected from the group consisting of silica, aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride and combinations thereof.

25. A thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is

electrically connected, or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, reaction products of which are capable of softening and losing adhesivensss comprising:

a curable resin component as set forth in Claim 1 in an amount in the range of from about 20% by weight to about 60% by weight, a curing agent component in an amount within the range of from about 1 to about 10% by weight, and optionally an anhydride component in an amount within the range of from about 10 to about 60% by weight, and optionally an inorganic filler component in an amount up to about 60% by weight.

26. Reaction products of the compositions in accordance with any one of Claims 1-25.

27. An electronic device comprising a semiconductor device and a circuit board to which said semiconductor device is electrically connected or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, assembled using a thermosetting resin composition according to any one of Claims 1-25 as an underfill sealant between the semiconductor device and the circuit board or the semiconductor chip and the circuit board, respectively, wherein reaction products of the composition are capable of softening and losing their adhesiveness under exposure to temperature conditions in excess of those used to cure the composition.

28. A method of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said

semiconductor device is electrically connected or a semiconductor chip and a circuit board to which said semiconductor chip is electrically connected, the steps of which comprise:

(a) dispensing into the underfilling between the semiconductor device and the circuit board or the semiconductor chip and the circuit board a composition in accordance with any one of Claims 1-25; and

(b) exposing the composition as so dispensed to conditions appropriate to cause the composition to form a reaction product.

29. A method of reworking a reaction product of a composition in accordance with any one of Claims 1-25, a step of which comprises:

(a) exposing the reaction product to conditions appropriate to cause the reaction product to soften and lose adhesiveness.

30. The method according to Claim 29, further comprising the steps of:

(b) removing the semiconductor chip or semiconductor device from the circuit board; and

(c) optionally, cleaning the surface of the circuit board to remove any cured reaction product that remains.

FIG. 1

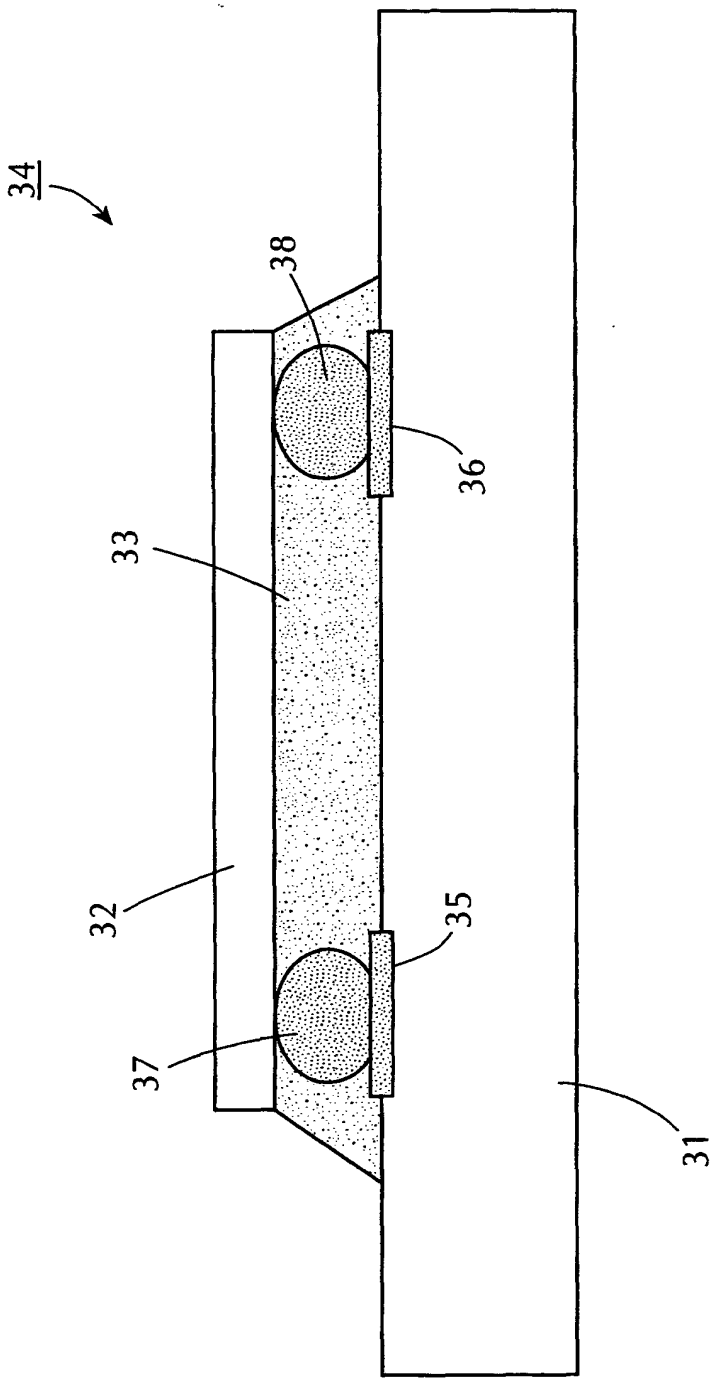


FIG. 2

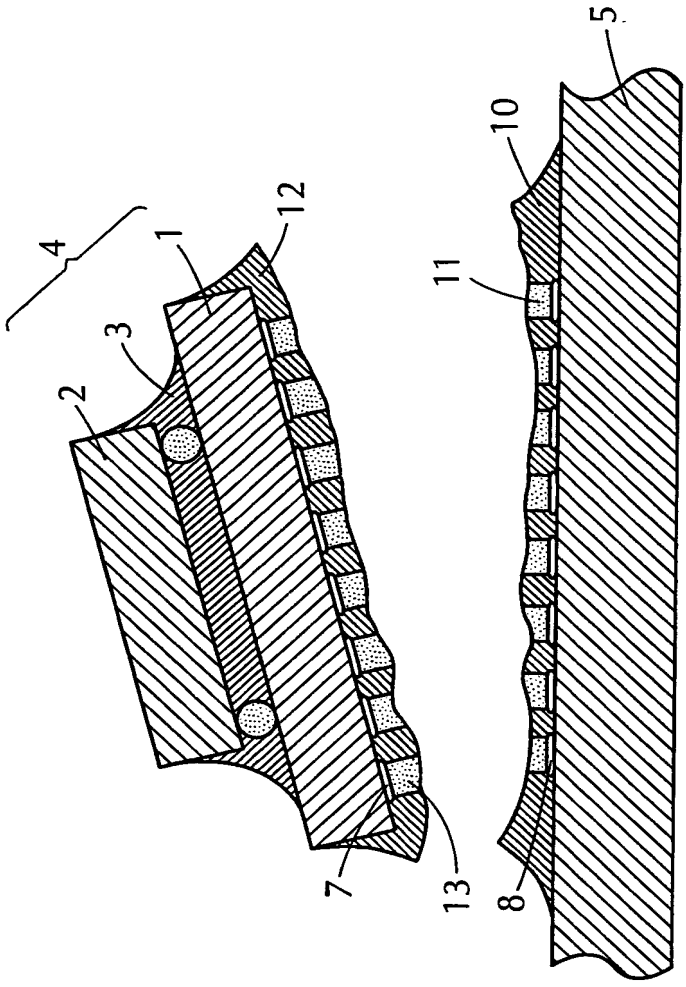


FIG. 3

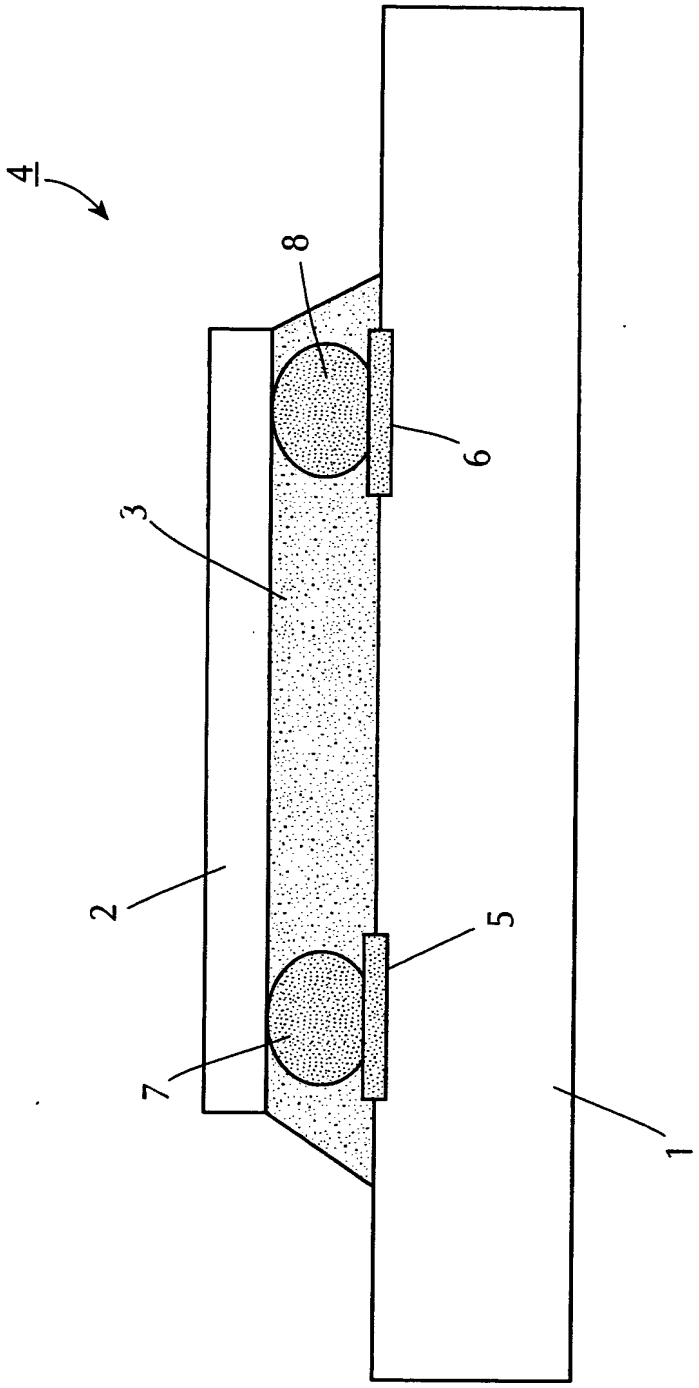


FIG. 4

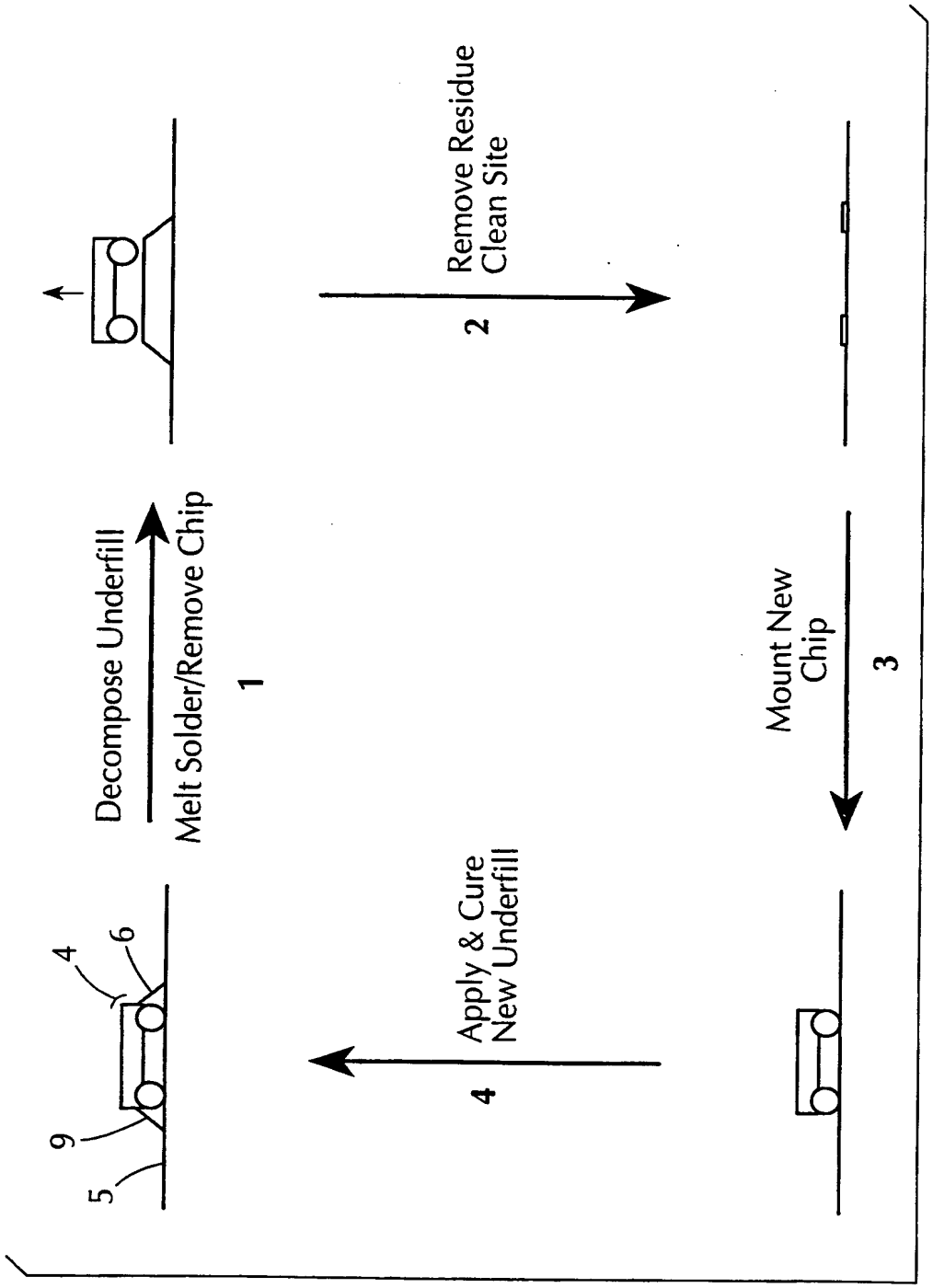

Decompose Underfill
Melt Solder/Remove Chip
1
Remove Residue
Clean Site
2
Mount New
Chip
3
Apply & Cure
New Underfill
4
4
6
9
5

FIG. 5

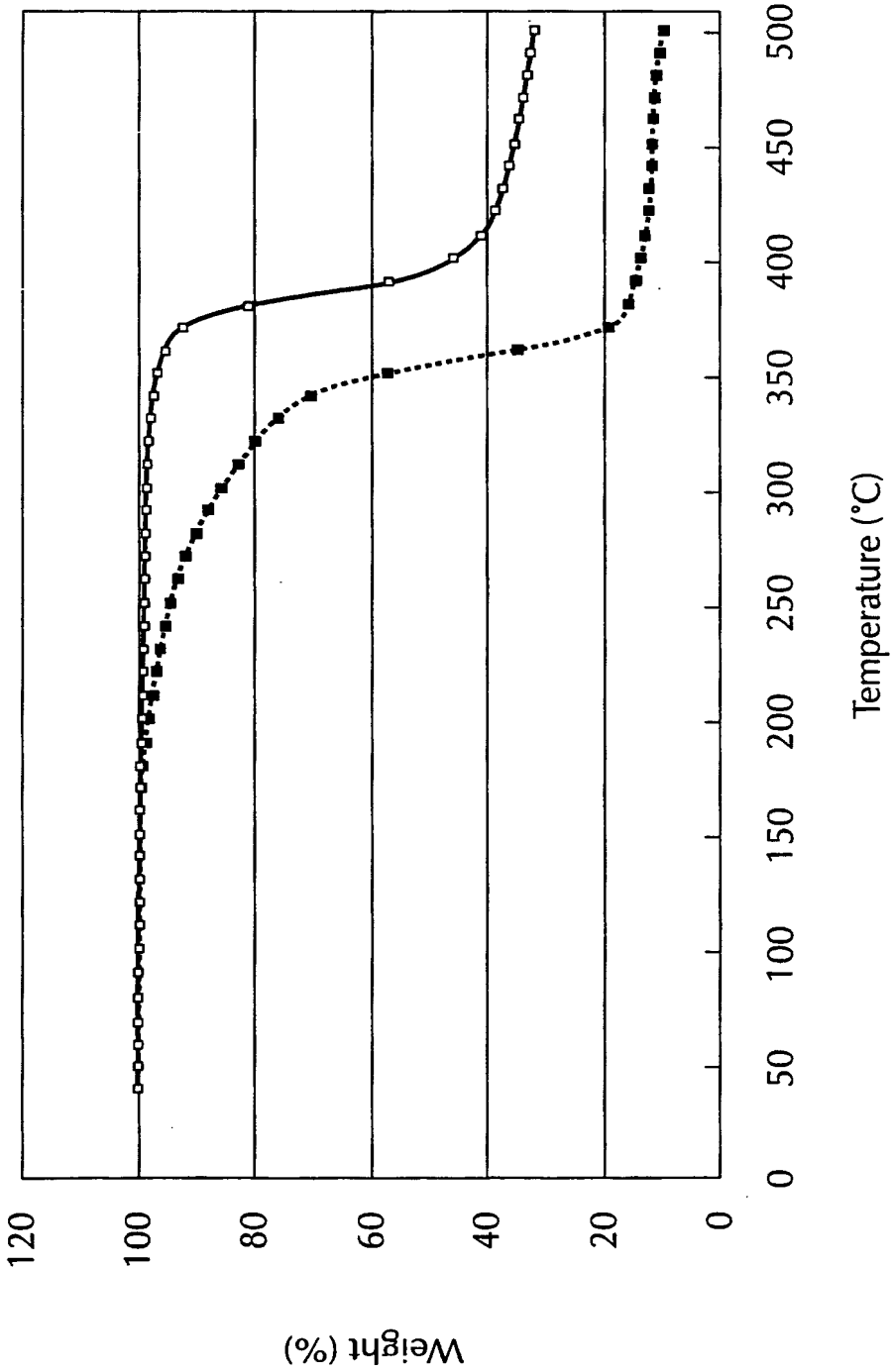

Weight (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

FIG. 6

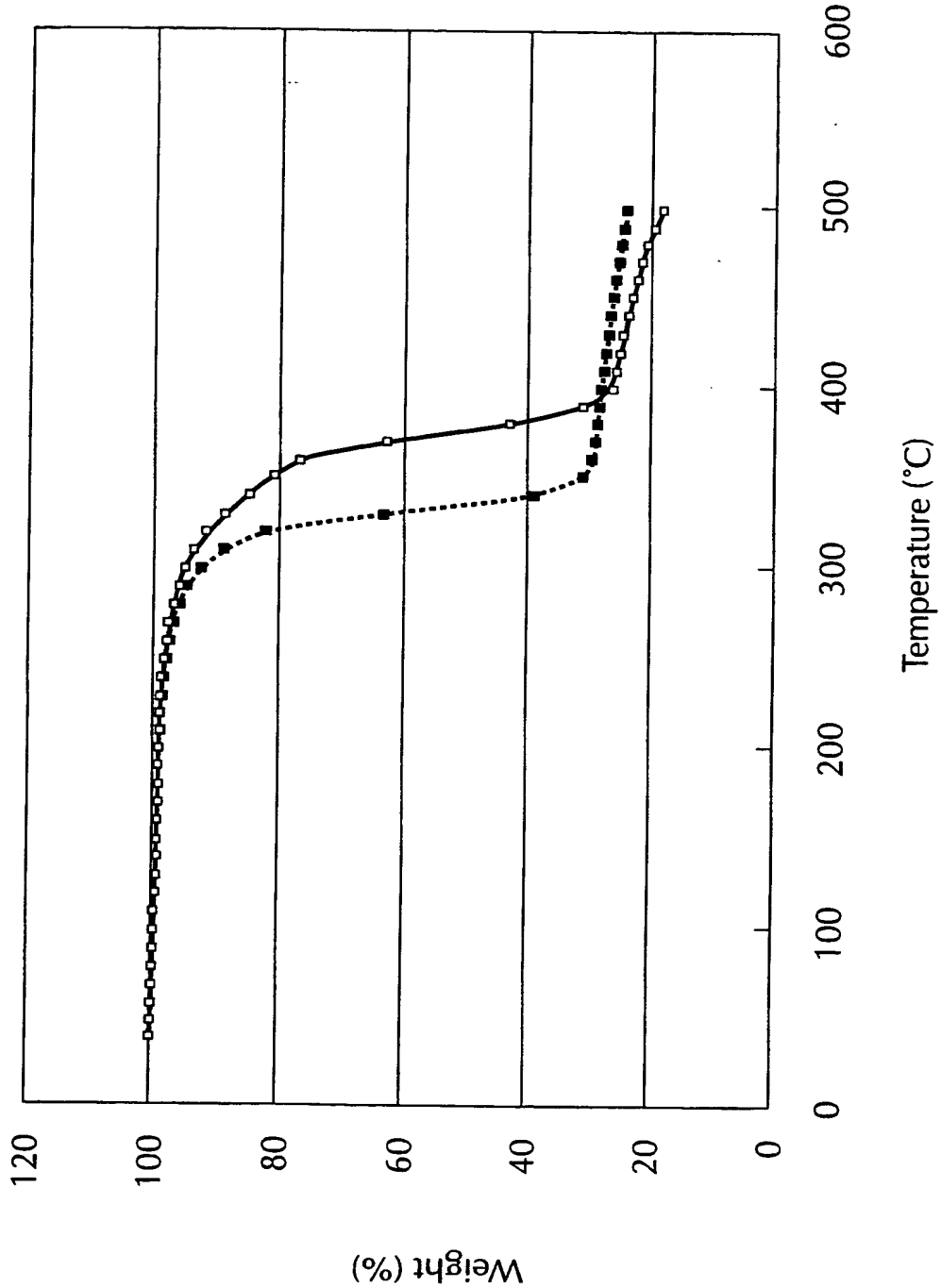

Weight (%)
120
100
80
60
40
20
0
0
100
200
300
400
500
600
Temperature (°C)

FIG. 7

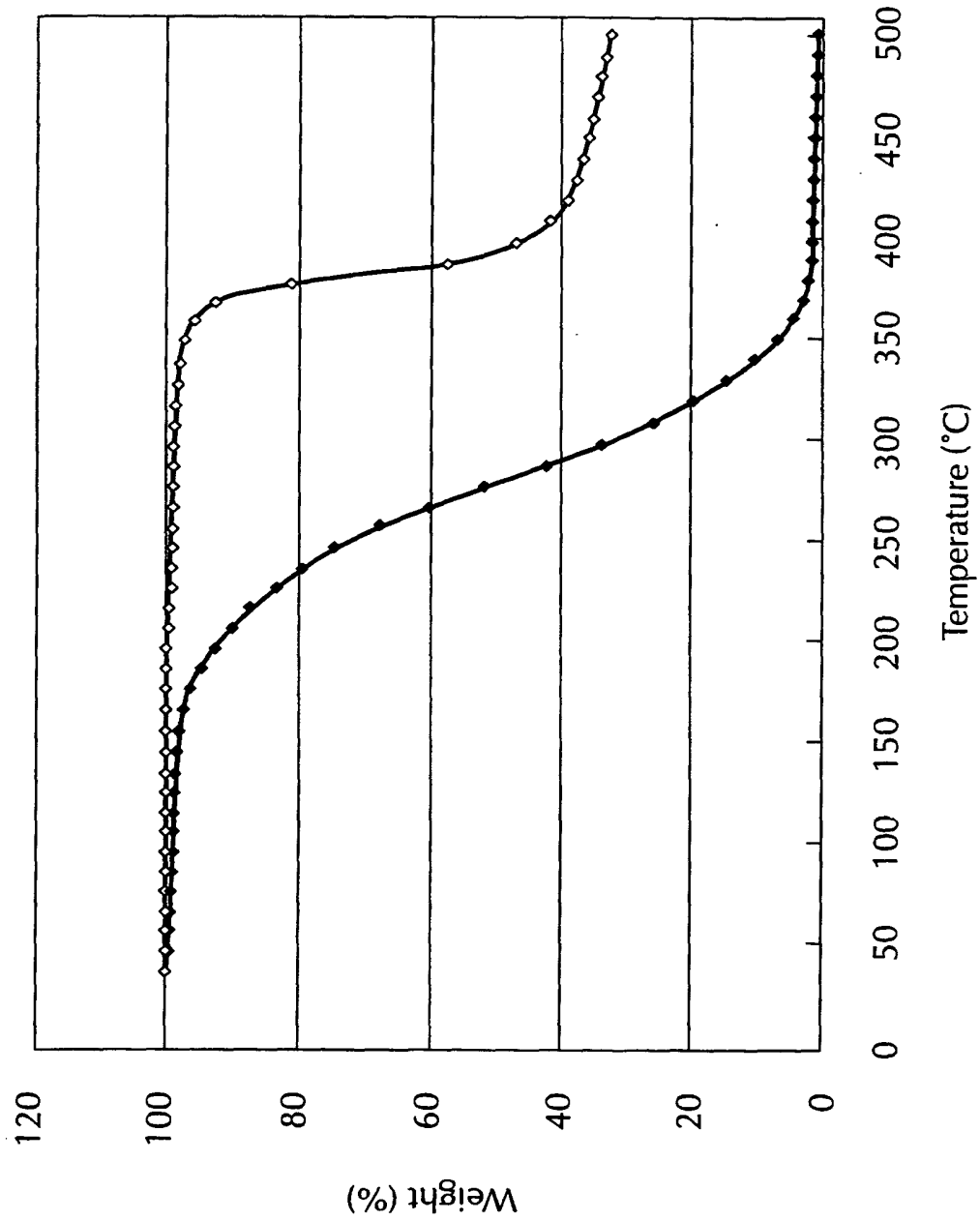

Weight (%)
120
100
80
60
40
20
0
0
50
100
150
200
250
300
350
400
450
500
Temperature (°C)

FIG. 8

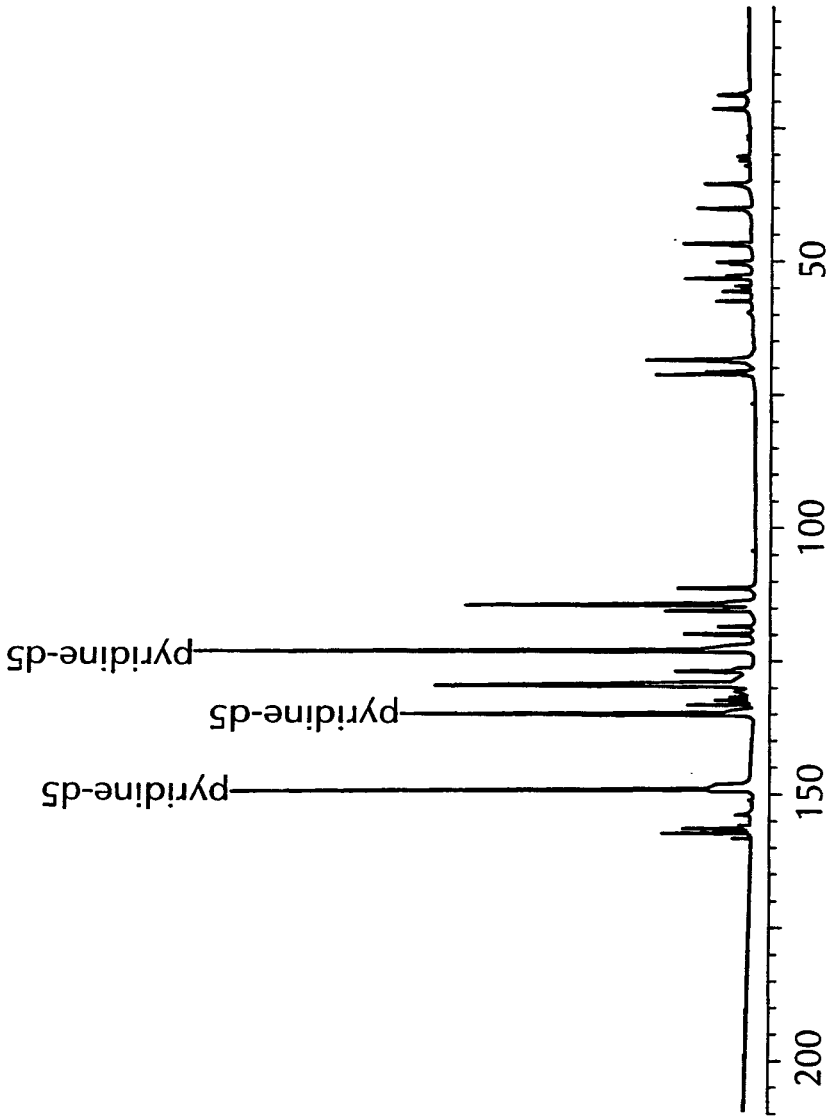
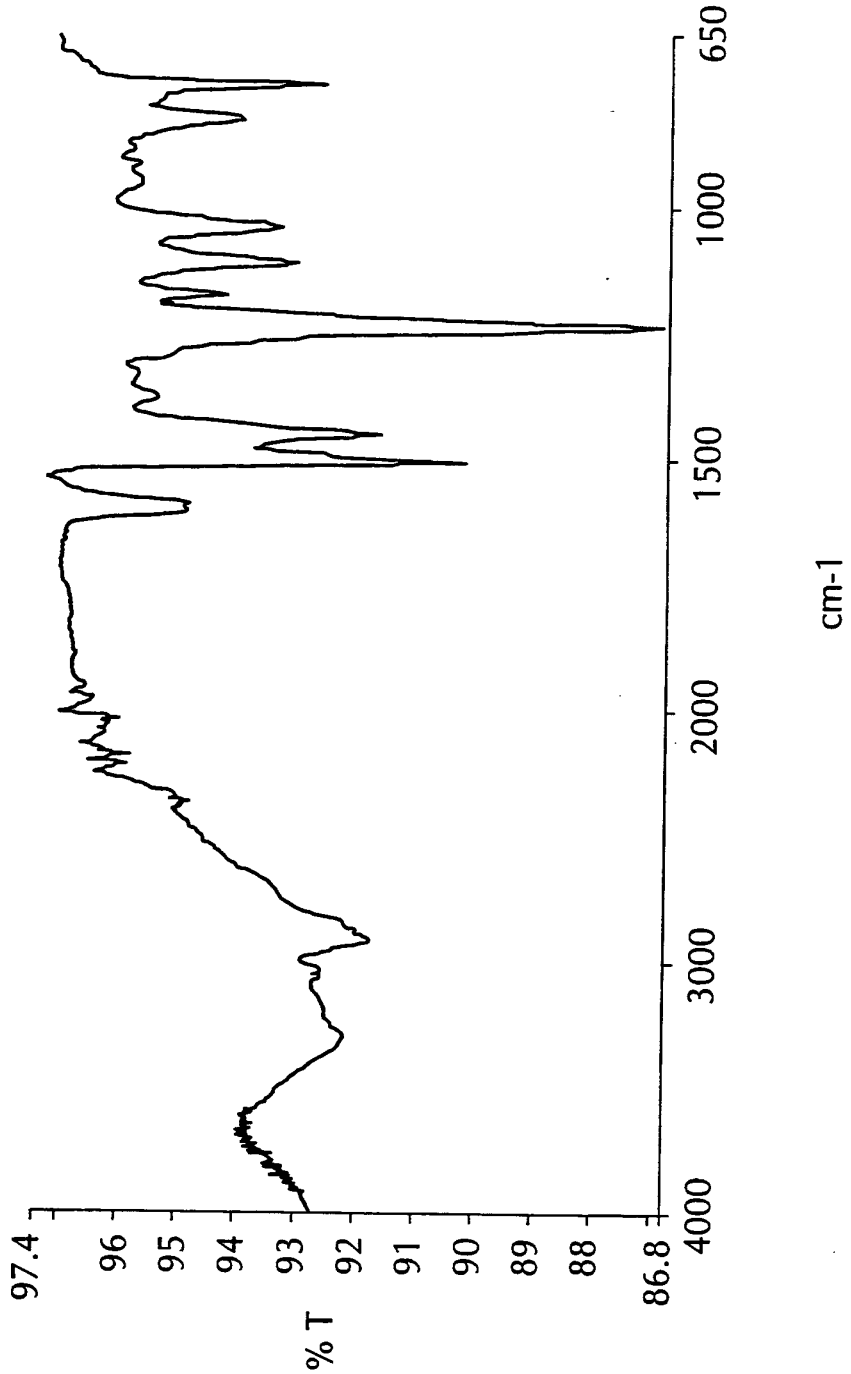


FIG. 9


97.4
96
95
94
93
92
91
90
89
88
86.8
% T
4000
3000
2000
1500
1000
650
cm-1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,512,613 A (AFZALI-ARDAKANI et al.) 30 April 1996, columns 9-10, Example 7 and column 14, Example 23.	1-3, 13, 17, 18 and 23-30
Y,P	US 5,932,682 A (BUCHWALTER et al.) 03 August 1999, column 9, Example 2B and column 10, Examples 6 and 7.	1-3, 13, 17, 18 and 23-30
Y,P	US 6,008,266 A (KUCZYNSKI et al.) 28 December 1999, columns 11-12, Examples 1A and 1B.	1, 3 and 24-30
Y	JP 11-17074 A (JSR CO., LTD., JAPAN) 26 June 1997, abstracts.	1, 3 and 24-30
Y	JP 08-12741 A (NEW JAPAN CHEM CO LTD) 16 January 1996, abstract.	1-3 and 24-30

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
01 SEPTEMBER 2000	01 NOV 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT SELLERS Telephone No. (703) 308-2399

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 09-316421 A (SUMITOMO SEIKA K. K., JAPAN) 09 December 1997, abstract.	1
Y	JP 58-42290 A (HITACHI CHEMICAL CO., LTD., JAPAN) 03 November 1983, abstract.	1, 3 and 10
Y	JP 05-271389 A (TAIRU MENTO KK, JAPAN) 19 October 1993, abstracts.	1, 3, 10 and 24-30
Y	JP 02-18412 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 22 January 1990, abstracts.	1, 10, 13 and 24-30
Y	JP 63-159426 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 02 July 1988, abstract.	1-3 and 10
Y	JP 62-295029 A (HITACHI LTD., JAPAN) 22 December 1987, abstract.	1, 3, 10, 13, 17 and 18
Y	JP 06-136092 A (NEW JAPAN CHEM CO LTD) 17 May 1994, abstract.	1 and 10
Y	SERGEEV et al. Diglycidyl aromatic thio ethers and epoxy polymers derived from them. Vysokomol. Soedin., 1984, Vol. 26, No. 1, pages 208-211, abstract.	4-6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2 ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN-CAS: Files REG and CAPLUS. Search terms: Registry numbers for curable resin species disclosed on pages 11, 15 and 31 of the descrption. WEST: Files USPT, DWPI, JPAB, EPAB and IBM. Search terms: oxyalkylated epoxy resins, underfilling sealing, reworkable.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-26 and 28, drawn to a thermosetting resin composition and a method of sealing underfilling between a semiconductor device and a circuit board.
Group II, claims 1-26, 29 and 30, drawn to a thermosetting resin composition and a method of reworking a reaction product of the composition.
Group III, claim 27, drawn to an electronic device.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. The special technical feature is the composition of curable resin and a curing agent which is set forth in KUCZYNAKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The claimed composition does not make a contribution over the prior art, thereby establishing a lack of unity.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

1) The curable resins (a) of claims 4-12 comprising:
   i) Curable resins with a (thio)ether or carbonate core structure and pendant heteroatom-containing carbocyclic structures.
   ii) Alkylene oxide-containing epoxy resins.
   iii) An epoxy resin and a monoepoxy (thio)ester or carbonate coreactant diluent.

2) The curing agents (b) including amine compounds, amide compounds, imidazole compounds and their derivatives.

3) The compositions with and without the anhydride component.

The claims are deemed to correspond to the species listed above in the following manner:

1) Curable resins (a): Claims 4-12.
2) Curing agents (b): Claims 13-22.
3) Anhydride: Claims 2 and 23.

Claims 1-30 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features. The special technical feature is the composition of curable resin (a) and curing agent (b) which is disclosed in KUCZYNSKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The composition does not make a contribution over the prior art, thereby establishing a lack of unity between

the species.

The examination of all inventions and species has been elected.

PATENT COOPERATION TREATY

PCT

REC'D 31 AUG 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference ICC-196 PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/11878	International filing date *(day/month/year)* 16 JUNE 2000	Priority date *(day/month/year)* 17 JUNE 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant LOCTITE CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

   I [X] Basis of the report

   II [ ] Priority

   III [ ] Non-establishment of report with regard to novelty, inventive step or industrial applicability

   IV [ ] Lack of unity of invention

   V [X] Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI [ ] Certain documents cited

   VII [ ] Certain defects in the international application

   VIII [X] Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08 DECEMBER 2000	11 JUNE 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer B. Hawkins for ROBERT SELLERS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/IPEA/409 (cover sheet) (July 1998)*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/11878

I. Basis f the report

1. With regard to the elements of the international application:*

☐ the international application as originally filed

☒ the description:
pages 1-40 , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the claims:
pages NONE , as originally filed
pages 41-51 , as amended (together with any statement) under Article 19
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the drawings:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the sequence listing part of the description:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. 13

☒ the drawings, sheets/~~fig~~ NONE

5. ☒ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/11878

V. Reasoned statement under Article 35(2) with regard to n velty, inventive step or industrial applicability; citati ns and explanations supporting such statement

1. statement

Novelty (N)	Claims	7 and 10	YES
	Claims	1-6, 8, 9 and 11-30	NO
Inventive Step (IS)	Claims	7	YES
	Claims	1-6 and 8-30	NO
Industrial Applicability (IA)	Claims	1-30	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-4, 9 and 11-30 lack novelty under PCT Article 33(2) as being anticipated by U.S. Patent No. 5,512,613 (AFZALI-ARDAKANI et al.).

AFZALI-ADAKANI et al. (columns 9-10, Example 7 and column 14, Example 23) shows a cleavable composition for providing an underfill between a semiconductor chip and a substrate (column 7, lines 9-14 and 22-24) comprising a ketal diepoxide, an imidazole and hexahydrophthalic anhydride.

The arguments filed 14 May 2001 have been considered but are unpersuasive. Claim 1 encompasses a resin having at least two heteroatom-containing carbocyclic structures pending from an ether-containing core structure. Figures 1-3, particularly the last two structures, exhibit diepoxides with two ether group conforming to the claimed limitations.

Claims 1, 4-6, 8, 9 and 11-22 lack novelty under PCT Article 33(2) as being anticipated by the Vyoskomol. Soedin., Ser. A article by SERGEEV et al. entitled "Diglycidyl aromatic thio ethers and epoxy polymers derived from them."

SERGEEV et al. describes a composition containing bis[bis-4(2,3-epoxypropylthio)phenyl]sulfide and an aromatic S-containing diamine curing agent.

Claims 1, 4-6 and 9-22 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent Nos. 5-271389 (YONEZAWA et al.) or 2-18412 (OISHI et al.).

YONEZAWA et al. or OISHI et al. espouse compositions obtained from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 29-31 of the description) and a ketimine of a polyoxylalkylene diamine or triamine (YONEZAWA et al.) or a polyamideamine (OISHI et al.).

The arguments filed 14 May 2001 have been considered but are unpersuasive. The claimed controlled degradation "upon exposure to temperature conditions less than those used to cure said composition" is not recited. The structures of the ether and aromatic groups-containing diepoxides and amine or amide compound (Continued on Supplemental Sheet.)

VIII. Certain observations on the internati nal application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

The description is objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 5 because it fails to contain an adequate written description of ANCAMINE 2337S. The description is inadequate because there is no unequivocal structural identification, nor is the given description chemically accurate. Page 19, line 32 to page 20, line 3 indicates that "It is believed that 'ANCAMINE' 2337S is a novolac-type resin that has been modified through reaction with aliphatic amines, such as polyamines, pyrazines, pyridines, pyroles [sic] and pyrazoles."

The description of the reactants based on a mere belief does not enable one skilled in the art to make the curing agent. It is unclear how the amine groups of the aliphatic amine can react with the phenolic hydroxyl groups of the novolac-type resin to produce the curing agent.

Claims 20 and 21 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

The denotation of the species of modified amine compounds as "ANCAMINE" 2337S in claim 20 does not concisely represent the curing agent since tradenames are transient.

The term "type" used to characterize the "novolac-type resin" is not clearly defined. It cannot be ascertained what derivatives and/or modifications of the novolac are contemplated within the metes and bounds of the word "type."

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

CLASSIFICATION:
The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00 and US Cl.: 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

I. BASIS OF REPORT:

5. (Some) amendments are considered to go beyond the disclosure as filed:
The amendment of the claims filed 14 May 2001 is objected to under PCT Article 34(2)(b) because it adds matter into the application that goes beyond the disclosure as originally filed. The added new matter is the qualification in claim 1, lines 3-4 of the controlled degradability "upon exposure to temperature conditions less than those used to cure said composition." Page 7, lines 11-14 of the description indicates controlled degradability "by exposure to temperature conditions in excess of those used to cure the composition."
There is no support on page 17, lines 26-28 for the modified amide compounds as a species of curing agent (b).

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
curing agents of the references are clearly within the purview of the claims and inherently possesses controlled degradation at temperatures below cure.

Claims 1-6 and 9-30 lack an inventive step under PCT Article 33(3) as being obvious over Japanese Patent No. 8-12741 (NEW JAPAN CHEM CO LTD) in view of Japanese Patent No. 62-295029 (MATSUYAMA).
NEW JAPAN CHEM CO LTD discloses an impregnant for electronic parts prepared from 1,4-cyclohexane dimethanol diglycidyl ether, a curing promotor and an anhydride. The claimed species of curing agent is not recited. MATSUYAMA set forth a sealant derived from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 20-21 of the description), a novolak phenolic resin hardener, an imidazole accelerator and an aluminum oxide filler.
It would have been obvious to employ the imidazole of MATSUYAMA as the curing promotor of NEW JAPAN CHEM CO LTD in order to reduce the curing time and/or temperature.

Japanese Patent Nos. 11-17074 (CHIBA et al.), 9-316421 (YAMAMOTO et al.) and the CRIVELLO et al. article are withdrawn in response to the claims limited to certain species of curing agent which preclude the aromatic sulfonium salt curing catalyst of the prior art.

Japanese Patent Nos. 58-42290 (HITACHI CHEMICAL CO., LTD.), 63-159426 (SUMITOMO BAKELITE CO., LTD.) and 6-136092 (YAMANAKA et al.) are withdrawn since the claimed limitation defining controlled degradation "upon exposure to temperature conditions less than those used to cure said composition" is peculiar to its utility as a sealant for a semiconductor device which is not recited in the references.

Claim 7 meets the criteria set out in PCT Article 33(2) and 33(3) due to the lack of recitation of the carbonate diepoxide structure.

Claims 1-30 meet the criteria set out in PCT Article 33(4) due to the industrial applicability of the composition as an underfill sealant for a semiconductor device.

---------- NEW CITATIONS ----------
JP 10-1657 A2 (SHINKO CHEMICAL CO., LTD.) 06 January 1998, abstract identifying Sanaid SI 60L of JP 9-3164221 A2 as an aromatic sulfonium salt.

CRIVELLO et al. Structure and reactivity relationships in the photoinitiated cationic polymerization of oxetane monomers. J. Macromol. Sci., Pure Appl. Chem. 1993, Vol. A30, No. 2-3, pages 189-206, Chemical abstract accession no. 1993:7419 and Chemical abstract registry no. 60763-95-3P.

PJP
11/8/00

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

Applicant's or agent's file reference ICC-196 PCT	Date of Mailing *(day/month/year)* 01 NOV 2000 **FOR FURTHER ACTION** **See paragraphs 1 and 4 below**
International application No. PCT/US00/11878	International filing date *(day/month/year)* 16 JUNE 2000
Applicant LOCTITE CORPORATION	

1. [X] The applicant is hereby notified that the international search report has been established and is transmitted herewith.

   Filing of amendments and statement under Article 19:
   The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

   When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

   Where? Directly to the International Bureau of WIPO
   34, chemin des Colombettes
   1211 Geneva 20, Switzerland
   Facsimile No.: (41-22) 740.14.35

   For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

   [ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

   [ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

   Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 *bis* 1 and 90 *bis* 3, respectively, before the completion of the technical preparations for international publication.

   Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

   Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT SELLERS Telephone No. (703) 308-2399

Form PCT/ISA/220 (July 1998)★

(See notes on accompanying sheet)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference ICC-196 PCT	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US00/11878	International filing date *(day/month/year)* 16 JUNE 2000	(Earliest) Priority Date *(day/month/year)* 17 JUNE 1999
Applicant LOCTITE CORPORATION		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 7 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readable form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [X] **Unity of invention is lacking** (See Box II).

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   The title does not conform to PCT Rule 4.3: CONTROLLABLY DEGRADABLE COMPOSITION OF HETEROATOM CARBOCYCLIC OR EPOXY RESIN AND CURING AGENT

5. With regard to the **abstract,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. 1

   [X] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Box III TEXT OF THE ABSTRACT (Continuation of item 5 of the first sheet)

The technical problem and the gist of its solution are not presented (PCT Rule 8.1(a)(i)). The technical features mentioned in the abstract do not include a reference sign between parentheses (PCT Rule 8.1(d)). The following new abstract is proposed.

NEW ABSTRACT

A reworkable underfilling sealing material (33) for the attachment of a semiconductor device (32) to a carrier substrate (31) is prepared from a composition comprising a curable resin (a) which is a resin with a (thio)ether or carbonate core structure and a heteroatom-containing carbocyclic structure, an epoxy resin having at least one alkylene oxide residue, or an epoxy resin with a monoepoxide (thio)ester or carbonate coreactant diluent; and (b) a curing agent including a polyamine, an epoxy- or novolac-modified amine, an amide compound or an imidazole; optionally with an anhydride.

INTERNATIONAL SEARCH REPORT

International application No.
T/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,512,613 A (AFZALI-ARDAKANI et al.) 30 April 1996, columns 9-10, Example 7 and column 14, Example 23.	1-3, 13, 17, 18 and 23-30
Y,P	US 5,932,682 A (BUCHWALTER et al.) 03 August 1999, column 9, Example 2B and column 10, Examples 6 and 7.	1-3, 13, 17, 18 and 23-30
Y,P	US 6,008,266 A (KUCZYNSKI et al.) 28 December 1999, columns 11-12, Examples 1A and 1B.	1, 3 and 24-30
Y	JP 11-17074 A (JSR CO., LTD., JAPAN) 26 June 1997, abstracts.	1, 3 and 24-30
Y	JP 08-12741 A (NEW JAPAN CHEM CO LTD) 16 January 1996, abstract.	1-3 and 24-30

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* *Special categories of cited documents:*

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
01 SEPTEMBER 2000	01 NOV 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer ROBERT SELLERS Telephone No. (703) 308-2399

Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 09-316421 A (SUMITOMO SEIKA K. K., JAPAN) 09 December 1997, abstract.	1
Y	JP 58-42290 A (HITACHI CHEMICAL CO., LTD., JAPAN) 03 November 1983, abstract.	1, 3 and 10
Y	JP 05-271389 A (TAIRU MENTO KK, JAPAN) 19 October 1993, abstracts.	1, 3, 10 and 24-30
Y	JP 02-18412 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 22 January 1990, abstracts.	1, 10, 13 and 24-30
Y	JP 63-159426 A (SUMITOMO BAKELITE CO., LTD., JAPAN) 02 July 1988, abstract.	1-3 and 10
Y	JP 62-295029 A (HITACHI LTD., JAPAN) 22 December 1987, abstract.	1, 3, 10, 13, 17 and 18
Y	JP 06-136092 A (NEW JAPAN CHEM CO LTD) 17 May 1994, abstract.	1 and 10
Y	SERGEEV et al. Diglycidyl aromatic thio ethers and epoxy polymers derived from them. Vysokomol. Soedin., 1984, Vol. 26, No. 1, pages 208-211, abstract.	4-6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/11878

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

STN-CAS: Files REG and CAPLUS. Search terms: Registry numbers for curable resin species disclosed on pages 11, 15 and 31 of the descrption. WEST: Files USPT, DWPI, JPAB, EPAB and IBM. Search terms: oxyalkylated epoxy resins, underfilling sealing, reworkable.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-26 and 28, drawn to a thermosetting resin composition and a method of sealing underfilling between a semiconductor device and a circuit board.
Group II, claims 1-26, 29 and 30, drawn to a thermosetting resin composition and a method of reworking a reaction product of the composition.
Group III, claim 27, drawn to an electronic device.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. The special technical feature is the composition of curable resin and a curing agent which is set forth in KUCZYNAKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The claimed composition does not make a contribution over the prior art, thereby establishing a lack of unity.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

1) The curable resins (a) of claims 4-12 comprising:
   i) Curable resins with a (thio)ether or carbonate core structure and pendant heteroatom-containing carbocyclic structures.
   ii) Alkylene oxide-containing epoxy resins.
   iii) An epoxy resin and a monoepoxy (thio)ester or carbonate coreactant diluent.

2) The curing agents (b) including amine compounds, amide compounds, imidazole compounds and their derivatives.

3) The compositions with and without the anhydride component.

The claims are deemed to correspond to the species listed above in the following manner:

1) Curable resins (a): Claims 4-12.
2) Curing agents (b): Claims 13-22.
3) Anhydride: Claims 2 and 23.

Claims 1-30 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features. The special technical feature is the composition of curable resin (a) and curing agent (b) which is disclosed in KUCZYNSKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The composition does not make a contribution over the prior art, thereby establishing a lack of unity between

the species.

The examination of all inventions and species has been elected.

ATENT COOPERATION TREA

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067

PJP
9/4/01

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

	Date of Mailing *(day/month/year)*
Applicant's or agent's file reference ICC-196 PCT	IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority Date *(day/month/year)*
PCT/US00/11878	16 JUNE 2000	17 JUNE 1999

Applicant
LOCTITE CORPORATION

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ROBERT SELLERS for B. Foudin
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/IPEA/416 (July 1992)★

ATENT COOPERATION TREA

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067

PCT

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of Mailing *(day/month/year)*	28 AUG 2001

Applicant's or agent's file reference	IMPORTANT NOTIFICATION
ICC-196 PCT	

International application No.	International filing date *(day/month/year)*	Priority Date *(day/month/year)*
PCT/US00/11878	16 JUNE 2000	17 JUNE 1999

Applicant
LOCTITE CORPORATION

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ROBERT SELLERS for B. Hawkins
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/IPEA/416 (July 1992)★

ATENT COOPERATION TREA

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference ICC-196 PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/11878	International filing date *(day/month/year)* 16 JUNE 2000	Priority date *(day/month/year)* 17 JUNE 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant LOCTITE CORPORATION		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets.

   [X] This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 10 sheets.

3. This report contains indications relating to the following items:

   I [X] Basis of the report

   II [ ] Priority

   III [ ] Non-establishment of report with regard to novelty, inventive step or industrial applicability

   IV [ ] Lack of unity of invention

   V [X] Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI [ ] Certain documents cited

   VII [ ] Certain defects in the international application

   VIII [X] Certain observations on the international application

Date of submission of the demand	Date of completion of this report
08 DECEMBER 2000	11 JUNE 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer ROBERT SELLERS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/IPEA/409 (cover sheet) (July 1998)*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/11878

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed

☒ the description:
pages 1-40 , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the claims:
pages NONE , as originally filed
pages 41-51 , as amended (together with any statement) under Article 19
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the drawings:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

☒ the sequence listing part of the description:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE

☒ the claims, Nos. 13

☒ the drawings, sheets/~~fig~~ NONE

5. ☒ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/11878

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	7 and 10	YES
	Claims	1-6, 8, 9 and 11-30	NO
Inventive Step (IS)	Claims	7	YES
	Claims	1-6 and 8-30	NO
Industrial Applicability (IA)	Claims	1-30	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-4, 9 and 11-30 lack novelty under PCT Article 33(2) as being anticipated by U.S. Patent No 5,512,613 (AFZALI-ARDAKANI et al.).

AFZALI-ADAKANI et al. (columns 9-10, Example 7 and column 14, Example 23) shows a cleavable composition for providing an underfill between a semiconductor chip and a substrate (column 7, lines 9-14 and 22-24) comprising a ketal diepoxide, an imidazole and hexahydrophthalic anhydride.

The arguments filed 14 May 2001 have been considered but are unpersuasive. Claim 1 encompasses a resin having at least two heteroatom-containing carbocyclic structures pending from an ether-containing core structure. Figures 1-3, particularly the last two structures, exhibit diepoxides with two ether group conforming to the claimed limitations.

Claims 1, 4-6, 8, 9 and 11-22 lack novelty under PCT Article 33(2) as being anticipated by the Vyoskomol. Soedin., Ser. A article by SERGEEV et al. entitled "Diglycidyl aromatic thio ethers and epoxy polymers derived from them."

SERGEEV et al. describes a composition containing bis[bis-4(2,3-epoxypropylthio)phenyl]sulfide and an aromatic S-containing diamine curing agent.

Claims 1, 4-6 and 9-22 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent Nos. 5-271389 (YONEZAWA et al.) or 2-18412 (OISHI et al.).

YONEZAWA et al. or OISHI et al. espouse compositions obtained from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 29-31 of the description) and a ketimine of a polyoxylalkylene diamine or triamine (YONEZAWA et al.) or a polyamideamine (OISHI et al.).

The arguments filed 14 May 2001 have been considered but are unpersuasive. The claimed controlled degradation "upon exposure to temperature conditions less than those used to cure said composition" is not recited. The structures of the ether and aromatic groups-containing diepoxides and amine or amide compound (Continued on Supplemental Sheet.)

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

The description is objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 5 because it fails to contain an adequate written description of ANCAMINE 2337S. The description is inadequate because there is no unequivocal structural identification, nor is the given description chemically accurate. Page 19, line 32 to page 20, line 3 indicates that "It is believed that 'ANCAMINE' 2337S is a novolac-type resin that has been modified through reaction with aliphatic amines, such as polyamines, pyrazines, pyridines, pyroles [sic] and pyrazoles."

The description of the reactants based on a mere belief does not enable one skilled in the art to make the curing agent. It is unclear how the amine groups of the aliphatic amine can react with the phenolic hydroxyl groups of the novolac-type resin to produce the curing agent.

Claims 20 and 21 are objected to as lacking clarity under PCT Rule 66.2(a)(v) because practice of the claimed invention is not adequately described in writing, as required under PCT Rule 5.1(a)(iii), for the reasons set forth in the immediately preceding paragraph.

The denotation of the species of modified amine compounds as "ANCAMINE" 2337S in claim 20 does not concisely represent the curing agent since tradenames are transient.

The term "type" used to characterize the "novolac-type resin" is not clearly defined. It cannot be ascertained what derivatives and/or modifications of the novolac are contemplated within the metes and bounds of the word "type."

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00 and US Cl.: 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

I. BASIS OF REPORT:

5. (Some) amendments are considered to go beyond the disclosure as filed:

The amendment of the claims filed 14 May 2001 is objected to under PCT Article 34(2)(b) because it adds matter into the application that goes beyond the disclosure as originally filed. The added new matter is the qualification in claim 1, lines 3-4 of the controlled degradability "upon exposure to temperature conditions less than those used to cure said composition." Page 7, lines 11-14 of the description indicates controlled degradability "by exposure to temperature conditions in excess of those used to cure the composition."

There is no support on page 17, lines 26-28 for the modified amide compounds as a species of curing agent (b).

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
curing agents of the references are clearly within the purview of the claims and inherently possesses controlled degradation at temperatures below cure.

Claims 1-6 and 9-30 lack an inventive step under PCT Article 33(3) as being obvious over Japanese Patent No. 8-12741 (NEW JAPAN CHEM CO LTD) in view of Japanese Patent No. 62-295029 (MATSUYAMA).

NEW JAPAN CHEM CO LTD discloses an impregnant for electronic parts prepared from 1,4-cyclohexane dimethanol diglycidyl ether, a curing promotor and an anhydride. The claimed species of curing agent is not recited. MATSUYAMA set forth a sealant derived from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 20-21 of the description), a novolak phenolic resin hardener, an imidazole accelerator and an aluminum oxide filler.

It would have been obvious to employ the imidazole of MATSUYAMA as the curing promotor of NEW JAPAN CHEM CO LTD in order to reduce the curing time and/or temperature.

Japanese Patent Nos. 11-17074 (CHIBA et al.), 9-316421 (YAMAMOTO et al.) and the CRIVELLO et al. article are withdrawn in response to the claims limited to certain species of curing agent which preclude the aromatic sulfonium salt curing catalyst of the prior art.

Japanese Patent Nos. 58-42290 (HITACHI CHEMICAL CO., LTD.), 63-159426 (SUMITOMO BAKELITE CO., LTD.) and 6-136092 (YAMANAKA et al.) are withdrawn since the claimed limitation defining controlled degradation "upon exposure to temperature conditions less than those used to cure said composition" is peculiar to its utility as a sealant for a semiconductor device which is not recited in the references.

Claim 7 meets the criteria set out in PCT Article 33(2) and 33(3) due to the lack of recitation of the carbonate diepoxide structure.

Claims 1-30 meet the criteria set out in PCT Article 33(4) due to the industrial applicability of the composition as an underfill sealant for a semiconductor device.

---------- NEW CITATIONS ----------

JP 10-1657 A2 (SHINKO CHEMICAL CO., LTD.) 06 January 1998, abstract identifying Sanaid SI 60L of JP 9-3164221 A2 as an aromatic sulfonium salt.

CRIVELLO et al. Structure and reactivity relationships in the photoinitiated cationic polymerization of oxetane monomers. J. Macromol. Sci., Pure Appl. Chem. 1993, Vol. A30, No. 2-3, pages 189-206, Chemical abstract accession no. 1993:7419 and Chemical abstract registry no. 60763-95-3P.

CHAPTER I
PCT TELEPHONE MEMORANDUM
FOR
LACK OF UNITY OF INVENTION

PCT No.: PCT/US00/11878

Examiner: ROBERT SELLERS

Attorney spoken to: STEVEN C. BAUMAN

Date of call: 18 AUGUST 2000

- ☒ Amount of payment approved: $420.00
- ☒ Deposit account number to be charged: 12-2135
- ☒ Attorney elected to pay for ALL additional inventions
- ☐ Attorney elected to pay only for the additional inventions covered by
  - ☐ Group(s):

-- encompassing --

  - ☐ Claim(s):

- ☐ Attorney elected NOT to pay for any additional inventions, therefore, only the first claimed invention (Group I) covered by Claim(s) _ has been searched.
- ☒ Attorney was orally advised that there is no right to protest for any group not paid for.
- ☒ Attorney was orally advised that any protest must be filed no later than 15 days from the mailing of the Search Report (PCT/ISA/210).

Time Limit For Filing A Protest

Applicant is hereby given 15 days from the mailing date of this Search Report in which to file a protest of the holding of lack of unity of invention. In accordance with PCT Rule 40.2, applicant may protest the holding of lack of unity only with respect to the group(s) paid for.

Detailed Reasons For Holding Lack Of Unity Of Invention:

Detailed Reasons For Holding Lack of Unity Of Invention:
(Continued on a separate sheet)

Note: A copy of this form must be attached to the Search Report.

ATTACHM TO CHAPTER I PCT TELEPHON[redacted]EMORANDUM FOR LACK OF UNITY OF INVENTION

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-26 and 28, drawn to a thermosetting resin composition and a method of sealing underfilling between a semiconductor device and a circuit board.
Group II, claims 1-26, 29 and 30, drawn to a thermosetting resin composition and a method of reworking a reaction product of the composition.
Group III, claim 27, drawn to an electronic device.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. The special technical feature is the composition of curable resin and a curing agent which is set forth in KUCZYNAKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The claimed composition does not make a contribution over the prior art, thereby establishing a lack of unity.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

1) The curable resins (a) of claims 4-12 comprising:
   i) Curable resins with a (thio)ether or carbonate core structure and pendant heteroatom-containing carbocyclic structures.
   ii) Alkylene oxide-containing epoxy resins.
   iii) An epoxy resin and a monoepoxy (thio)ester or carbonate coreactant diluent.

2) The curing agents (b) including amine compounds, amide compounds, imidazole compounds and their derivatives.

3) The compositions with and without the anhydride component.

The claims are deemed to correspond to the species listed above in the following manner:

1) Curable resins (a): Claims 4-12.
2) Curing agents (b): Claims 13-22.
3) Anhydride: Claims 2 and 23.

Claims 1-30 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features. The special technical feature is the composition of curable resin (a) and curing agent (b) which is

ATTACHME[redacted]TO CHAPTER I PCT TELEPHON[redacted]EMORANDUM
FOR
LACK OF UNITY OF INVENTION

disclosed in KUCZYNSKI et al. and Japanese Patent Nos. 11-17074 and 8-12741. The composition does not make a contribution over the prior art, thereby establishing a lack of unity between the species.

The examination of all inventions and species has been elected.

PCT INTERNATIONAL APPLICATION TRANSMITTAL LETTER DATE: June 14, 2000 10/009818

REGARDING THE INTERNATIONAL APPLICATION OF DOCKET OR REFERENCE NUMBER: ICC-196/PCT
LOCTITE CORPORATION and DOBA, Taka[redacted]

ENTITLED
Reworkable Thermosetting Resin Compositions 13 DEC 2001

Certification under 37 CFR 1.10 (if applicable)

"Express Mail" mailing number _____ Date of Deposit _____

I hereby certify that this application is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Commissioner of Patents and Trademarks, Box PCT, Washington, D.C. 20231.

(Typed or printed name of person mailing application) _____ (Signature of person mailing application) _____

To the United States Receiving Office (RO/US):

Accompanying this transmittal letter is the above-identified international application, including a completed Request form (PCT/RO/101). Please process the application according to the provisions of the Patent Cooperation Treaty.

The following requests are made of the RO/US:

1. ☒ PREPARATION AND TRANSMITTAL OF CERTIFIED COPY OF PRIORITY DOCUMENTS -- Please prepare and transmit to the International Bureau a certified copy of the United States origin priority documents identified in Box VI of the Request form (37 CFR 1.451).

   To cover the cost of copy preparation and certification (37 CFR 1.19(a)(3) and (b)(1),
   ☐ a (check) (money order) in the amount of $_____ is attached to this transmittal letter.
   ☒ the RO/US is hereby authorized to charge the following deposit account no.: 12-2135.

   The appropriate Search fee for the above-named Authority is indicated on the Fee Calculation Sheet (PCT/RO/101 Annex).

2. ☒ SUPPLEMENTAL SEARCH FEES (ONLY WHEN ISA/US CONDUCTS THE INTERNATIONAL SEARCH) -- Please charge any Supplemental Search fees that may be required by the United States International Searching Authority (ISA/US) to deposit account no.: 12-2135.

   I understand that this authorization is subject to my oral confirmation thereof in each instance and that it in no way limits my right to submit a protest against payment of the Supplemental Search fees, but is merely an administrative aid to assure that the ISA/US may timely complete the Search Report.

   NOTE: SUPPLEMENTAL SEARCH FEES FOR ISA/EP ARE PAYABLE DIRECTLY TO THE EUROPEAN PATENT OFFICE

3. ☒ DISCLOSURE INFORMATION -- In order to assist in screening the accompanying international application for purposes of determining whether a license for foreign transmittal should and could be granted and for other purposes, the following information is supplied:

   A. ☐ There is no prior filed application relating to this invention.

   B. ☒ There are prior applications, serial number 60/139,486 filed on June 17, 1999, serial number 60/193,392 filed on March 31, 2000, serial number 60/193,391 filed on March 31, 2000 and serial number NYA filed June 9, 2000.

      Which together contains subject matter that is

      1. ☐ substantially identical to that of the accompanying international application.
      2. ☒ less than that of the accompanying international application. The additional subject matter of the international application appears ~~on page(s) and lines(s)~~ throughout the application.
      3. ☐ more than that of the accompanying international application. The additional subject matter of the international application appears throughout the application.

   C. ☐ Disclosure information cannot be covered by the language of Points 3A or 3B above due to the involvement of several prior applications or for other reasons. A separate sheet on which the disclosure information is explained is attached to this transmittal letter.

4. ☒ REQUEST FOR FOREIGN TRANSMITTAL LICENSE -- According to the provisions of 35 U.S.C. 184 and 37 CFR 5.11, a license to transmit the accompanying international application to foreign agencies or international authorities is hereby requested.

*Priority is not claimed, unless all necessary information is listed in Box VI of the Request Form (PCT/RO/101).

SIGNER IS THE:
☐ APPLICANT
☐ COMMON REPRESENTATIVE
☒ (ATTORNEY) ~~(AGENT)~~
REG. NO. 33,832

NAME OF SIGNER (typed) Steven C. Bauman

Steven C. Bauman
SIGNATURE

PCT REQUEST ICC-196 PCT

Original (for **SUBMISSION**) - printed on 15.06.2000 08:04:50 AM

0	**For receiving Office use only**	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	**Form - PCT/RO/101 PCT Request**	
0-4-1	Prepared using	PCT-EASY Version 2.90 (updated 08.03.2000)
0-5	**Petition** The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	**Receiving Office (specified by the applicant)**	United States Patent and Trademark Office (USPTO) (RO/US)
0-7	**Applicant's or agent's file reference**	ICC-196 PCT
I	**Title of invention**	REWORKABLE THERMOSETTING RESIN COMPOSITIONS
II	**Applicant**	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	LOCTITE CORPORATION
II-5	Address:	LEGAL DEPARTMENT 1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America
II-6	State of nationality	US
II-7	State of residence	US
II-8	Telephone No.	(860) 571-5001
II-9	Facsimile No.	(860) 571-5028
III-1	**Applicant and/or inventor**	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	DOBA, Takahisa
III-1-5	Address:	3-18-7, Noukendai Kanazawa-Ku Yokohama, 236-0057 Japan
III-1-6	State of nationality	JP
III-1-7	State of residence	JP

PCT REQUEST ICC-196 PCT

Original (for **SUBMISSION**) - printed on 15.06.2000 08:04:50 AM

III-2	**Applicant and/or inventor**	
III-2-1	This person is:	applicant only
III-2-2	Applicant for	all designated States except US
III-2-4	Name	LOCTITE (JAPAN) CORPORATION
III-2-5	Address:	15-13 Fukuura 1-Chome Kanazawa-Ku Yokohama, 236 Japan
III-2-6	State of nationality	JP
III-2-7	State of residence	JP
IV-1	**Agent or common representative; or address for correspondence** The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	BAUMAN, Steven, C.
IV-1-2	Address:	Loctite Corporation 1001 Trout Brook Crossing Rocky Hill, CT 06067 United States of America
IV-1-3	Telephone No.	(860) 571-5001
IV-1-4	Facsimile No.	(860) 571-5028
V	**Designation of States**	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SL SZ TZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CR CU CZ DE DK DM DZ EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT TZ UA UG US UZ VN YU ZA ZW

PCT REQUEST ICC-196 PCT

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V-5	**Precautionary Designation Statement** In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	**Exclusion(s) from precautionary designations**	NONE	
VI-1	**Priority claim of earlier national application**		
VI-1-1	Filing date	17 June 1999 (17.06.1999)	
VI-1-2	Number	60/139,486	
VI-1-3	Country	US	
VI-2	**Priority claim of earlier national application**		
VI-2-1	Filing date	31 March 2000 (31.03.2000)	
VI-2-2	Number	60/193,392	
VI-2-3	Country	US	
VI-3	**Priority claim of earlier national application**		
VI-3-1	Filing date	31 March 2000 (31.03.2000)	
VI-3-2	Number	60/193,391	
VI-3-3	Country	US	
VI-4	**Priority claim of earlier national application**		
VI-4-1	Filing date	09 June 2000 (09.06.2000)	
VI-4-2	Number		
VI-4-3	Country	US	
VI-5	**Priority document request** The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1, VI-2, VI-3, VI-4	
VII-1	**International Searching Authority Chosen**	United States Patent and Trademark Office (USPTO) (ISA/US)	
VIII	**Check list**	number of sheets	electronic file(s) attached
VIII-1	Request	4	-
VIII-2	Description	40	-
VIII-3	Claims	9	-
VIII-4	Abstract	1	icc-196-pct_abstract.txt
VIII-5	Drawings	9	-
VIII-7	TOTAL	63	

PCT REQUEST ICC-196 PCT

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	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Return Receipt Postcard	-
VIII-18	**Figure of the drawings which should accompany the abstract**	1	
VIII-19	**Language of filing of the international application**	English	
IX-1	**Signature of applicant or agent**	Steven C. Bauman	
IX-1-1	Name (LAST, First)	BAUMAN, Steven, C.	

FOR RECEIVING OFFICE USE ONLY

10-1	**Date of actual receipt of the purported international application**	
10-2	**Drawings:**	
10-2-1	Received	
10-2-2	Not received	
10-3	**Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application**	
10-4	**Date of timely receipt of the required corrections under PCT Article 11(2)**	
10-5	**International Searching Authority**	ISA/US
10-6	**Transmittal of search copy delayed until search fee is paid**	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	**Date of receipt of the record copy by the International Bureau**	

PCT (ANNEX - FEE CALCULATION SHEET)

ICC-196 PCT

Original (for **SUBMISSION**) - printed on 15.06.2000 08:04:50 AM

(This sheet is not part of and does not count as a sheet of the international application)

0 0-1	**For receiving Office use only** International Application No.			
0-2	Date stamp of the receiving Office			
0-4 0-4-1	**Form - PCT/RO/101 (Annex)** **PCT Fee Calculation Sheet** Prepared using	PCT-EASY Version 2.90 (updated 08.03.2000)		
0-9	**Applicant's or agent's file reference**	ICC-196 PCT		
2	**Applicant**	LOCTITE CORPORATION, et al.		
12	**Calculation of prescribed fees**	fee amount/multiplier	total amounts (USD)	
12-1	Transmittal fee T	⇨	240	
12-2	Search fee S	⇨	700	
12-3	International fee Basic fee (first 30 sheets) b1	427		
12-4	Remaining sheets	33		
12-5	Additional amount (X)	10		
12-6	Total additional amount b2	330		
12-7	b1 + b2 = B	757		
12-8	Designation fees Number of designations contained in international application	85		
12-9	Number of designation fees payable (maximum 8)	8		
12-10	Amount of designation fee (X)	92		
12-11	Total designation fees D	736		
12-12	PCT-EASY fee reduction R	-132		
12-13	Total International fee (B+D-R) I	⇨	1,361	
12-14	Fee for priority document Number of priority documents requested	4		
12-15	Fee per document (X)	15		
12-16	Total priority document fee P	⇨	60	
12-17	**TOTAL FEES PAYABLE (T+S+I+P)**	⇨	2,361	
12-19	**Mode of payment**	authorization to charge deposit account		
12-20	**Deposit account instructions** The receiving Office:	United States Patent and Trademark Office (USPTO) (RO/US)		
12-20-1	is hereby authorized to charge the total fees indicated above to my deposit account	✓		
12-20-2	is hereby authorized to charge any deficiency or credit any over-payment in the total fees indicated above to my deposit account	✓		

PCT (ANNEX - FEE CALCULATION SHEET) ICC-196 PCT

Original (for **SUBMISSION**) - printed on 15.06.2000 08:04:50 AM

12-20-3	is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account	✓
12-21	Deposit account No.	12-2135
12-22	Date	15 June 2000 (15.06.2000)
12-23	Name and signature	BAUMAN, Steven, C. Steven C. Bauman

VALIDATION LOG AND REMARKS

13-2-3	Validation messages Names	Yellow Applicant 2.: JP Prefecture missing
		Yellow Applicant 3.: JP Prefecture missing
13-2-4	Validation messages Priority	Yellow Priority 4: Application No. is missing
13-2-6	Validation messages Contents	Yellow! The power of attorney or a copy of the general power of attorney will need to be furnished unless all applicants sign the request form.
13-2-8	Validation messages Payment	Green? Please ensure that you have a valid deposit account with the receiving Office selected.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 59/68, H01L 23/02 — A1

(11) International Publication Number: **WO 99/05196**

(43) International Publication Date: 4 February 1999 (04.02.99)

(21) International Application Number: PCT/US98/15578

(22) International Filing Date: 22 July 1998 (22.07.98)

(30) Priority Data:
60/053,592 24 July 1997 (24.07.97) US

(71) Applicant *(for all designated States except US)*: LOCTITE CORPORATION [US/US]; Hartford Square North, 10 Columbus Boulevard, Hartford, CT 06106–5108 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: KONARSKI, Mark [US/US]; 22 South Cove Road, Old Saybrook, CT 06475 (US). SZCZEPNIAK, Zbigniew, A. [PL/US]; Apartment 26, 29A Cedar Street, Meriden, CT 06450 (US).

(74) Agent: BAUMAN, Steven, C.; Loctite Corporation, Hartford Square North, 10 Columbus Boulevard, Hartford, CT 06106–5018 (US).

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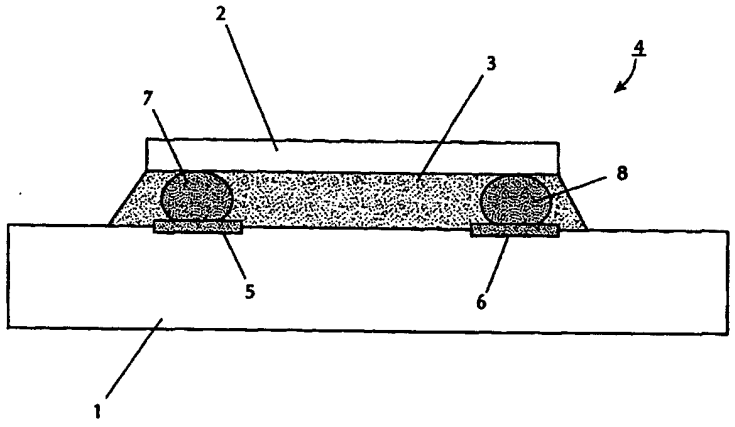

(57) Abstract

The present invention provides a thermosetting resin composition useful as an underfilling sealant composition which rapidly fills the underfill space in a semiconductor device, such as a flip chip assembly which includes a semiconductor chip mounted on a carrier substrate, enables the semi–conductor to be securely connected to a circuit board by short–time heat curing and with good productivity, and demonstrates acceptable heat shock properties (or thermal cycle properties). The thermosetting resin composition which is used as an underfilling sealant between such a semiconductor device and a circuit board to which the semiconductor device is electrically connected, includes an epoxy resin component and a latent hardener component. The latent hardener component includes a cyanate ester component and an imidizole component.

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THERMOSETTING RESIN COMPOSITIONS USEFUL AS UNDERFILL SEALANTS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to thermosetting resin compositions useful as underfill sealants for mounting under a circuit board direct chip attach ("DCA") packages, which have a semiconductor chip on a carrier substrate.

Brief Description of Related Technology

In recent years, the popularity of smaller-sized electronic appliances has made desirable size reduction of semiconductor devices. As a result, chip packages are becoming reduced in size to substantially that of the bare die themselves. Such smaller-sized chip packages improve the characteristics of the microelectronic device in which it is used, while retaining many beneficial operating features. This serves to protect semiconductor bare chips, and increases their reliability and useful life.

Ordinarily, chip assemblies are connected to electrical conductors on a circuit board by use of solder connection or the like. However, when the resulting

chip/circuit board structure is subjected to conditions of thermal cycling, reliability becomes suspect due to fatigue of the solder connection between the circuit board and the chip assembly. Recent manufacturing advances provide a sealing resin (often referred to as underfill sealant) in the space created by the mounting of a DCA [such as a chip scale package ("CSP")/ball grid array ("BGA") assembly] onto a circuit board to relieve stresses caused by thermal cycling. Underfill sealants have been seen to improve heat shock properties and enhance the reliability of such structures.

Of course, curable resin compositions generally are known. See e.g., U.S. Patent No. 4,645,803 (Kohli) which relates to curable epoxy resin compositions of reinforcing filaments and epoxy resins together with a primary amine-funtional curing agent with or without a polyamine curing agent and a curing catalyst which when cured into a fiber matrix is useful in preparing composites and prepreg materials for structural applications.

In addition, U.S. Patent No. 4,499,245 (Ikeguchi) relates to a curable resin composition requiring a mixture and/or a reaction product of (a) a polyfunctional cyanate ester, prepolymer of the cyanate ester or coprepolymer of the cyanate ester and an amine and (b) a polyhydantion resin -- a phenolic-based epoxy curative. In addition, a polyfunctional maleimide, prepolymer of the maleimide or coprepolymer of the maleimide and an amine may be included as a component (c). These compositions are reported to be useful as coating materials for rust prevention, flame resistance, flame retardation; electrical insulation varnish; and laminates for use with furniture, building materials, and sheathing materials.

And more specifically thermosetting compositions of cyanate esters and epoxy resins are also generally known. See e.g., Japanese patent document JP 62-275,123, an English-language abstract of which speaks to a resin composition for preparing prepreg materials with reinforcing fiber for structural applications. The compositions are

reported to include certain cyanate esters, bismaleimide, polyether sulfone (as a non-reactive thermoplast whose use is as a toughening agent) and bisphenol F- or A-type epoxy resin. In addition, the composition is reported to be optionally hardened by a hardening catalyst, one of which is noted as imidizole.

U.S. Patent No. 4,918,157 (Gardner) relates to the use of urea compounds as latent cure accelerators for cyanate esters, and to thermosetting cyanate ester formulations of cyanate esters and urea compounds. More specifically, the '157 patent claims a thermosetting composition of a cyanate ester; a urea compound selected from alkyl aryl ureas, aryl ureas and mixtures thereof; and an epoxy resin. The curable cyanate ester formulations of the '157 patent are reportedly useful as matrix resins, and for the production of prepreg, fiber-reinforced laminates, composites and the like.

Epoxy curing systems are also known. See e.g., U.S. Patent No. 3,862,260 (Sellers), in which a curing agent of a trifunctional hardener (such as the reaction product of one mole of bisphenol A with one mole of formaldehyde) and an imidizole is disclosed.

These uses for thermosetting resin compositions appear to be directed to structural applications, as contrasted to the microelectronic application to which the compositions of the present invention are directed. To that end, the use of epoxy resin compositions as matrix compositions for fiber reinforcement in prepreg, composite and laminate materials for structural materials differs significantly from the use of epoxy resin compositions as an adhesive and encapsulant in microelectronic applications, such as with electrical solder junctions in semiconductor chips, and creates different demands and requirements from the uncured resin as well as cured reaction products thereof.

A drawback to resin compositions presently used in microelectronics applications, such as for underfill sealants, is their extended cure schedule. In addition,

providing such resins with a commercially acceptable useful working life at room temperature or dispensing temperatures has been problematic.

Generally, at temperatures near room temperature, the resins begin to cure upon introduction of the curing agent or catalyst. This causes viscosity increases which leads to reduced dispensability. While such viscosity increase may be alleviated to some degree by using a liquid curing agent or catalyst, liquid catalysts tend to decrease latency to a point which is not commercially practical with current production demands. And introduction of a solid catalyst, such as imidizole, has limited applicability because its presence often changes the rheological properties of the composition, and decreases flow.

Thus, due at least in part to their extended cure schedules and limited useful working life, manufacturing capacity of certain microelectronic production lines has been hampered.

While seemingly simple, the solution to the problem of enhancing the cure speed of recently-used underfill sealants has ordinarily adversely impacted their useful working life. Thus, in the event that presently-used underfill sealants could be rendered more reactive, their useful working life may be further decreased, thereby removing the incentive to prepare a more reactive thermosetting resin composition for underfill sealing.

Accordingly, it would be desirable for an underfilling sealant composition to provide good adhesive properties while flowing and curing in a sufficiently quick time to be commercially appealing and possessing an extended useful working life.

SUMMARY OF THE INVENTION

The present invention provides a thermosetting resin composition useful as an underfilling sealant composition which (1) rapidly fills the underfill space in a semiconductor device, such as a flip chip assembly which includes a semiconductor chip mounted on a carrier

substrate, (2) enables the semiconductor to be securely connected to a circuit board by short-time heat curing and with good productivity, and (3) demonstrates excellent heat shock properties (or thermal cycle properties).

The thermosetting resin compositions of this invention which are used as underfill sealants between such a semiconductor device and a circuit board to which the semiconductor device is electrically connected, includes an epoxy resin component and a latent hardener component. The latent hardener component includes a cyanate ester component and an imidizole component.

By using the thermosetting resin compositions of this invention, semiconductor devices, such as flip chip assemblies, may be (1) assembled quickly and without production line down time because of improved cure speed and extended useful working life, and (2) securely connected to a circuit board by short-time heat curing of the composition, with the resulting mounted structure (at least in part due to the cured composition) demonstrating excellent heat shock properties (or thermal cycle properties).

The compositions of this invention may also be used for microelectronic applications beyond sealing underfill, such as with glob top, die attachment and other applications for thermosetting compositions in which rapid cure time and an extended useful working life are desirable.

The benefits and advantages of the present invention will become more readily apparent after a reading of the "Detailed Description of the Invention" together with the figure.

BRIEF DESCRIPTION OF THE FIGURE

Figure 1 depicts a cross-sectional view showing an example of a mounted structure with which the thermosetting resin composition of the present invention is used as an underfill sealant.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the thermosetting resin compositions which are useful as underfill sealants between a semiconductor device and a circuit board to which the semiconductor device is electrically connected, include an epoxy resin component and a latent hardener component. The latent hardener component includes a cyanate ester component and an imidizole component.

Typically, the composition includes about 100 parts by weight of the epoxy resin component, and 0 to about 30 parts by weight of the latent hardener component, of which 0 to about 15 parts is comprised of the cyanate ester component and 0 to about 15 parts is comprised of the imidizole component. Desirably, the latent hardener component should include about 4 parts each of the cyanate ester component and the imidizole component.

The epoxy resin component of the present invention may include any common epoxy resin. This epoxy resin may be comprised of at least one multifunctional epoxy resin, optionally, together with at least one monofunctional epoxy resin. Ordinarily, the multifunctional epoxy resin should be included in amount within the range of about 20 parts to about 100 parts of the epoxy resin component. In the case of bisphenol F-type epoxy resin, desirably the amount thereof should be in the range of from about 40 to 80 parts.

A monofunctional epoxy resin, if present, should ordinarily be used as a reactive diluent, or crosslink density modifier. In the event such a monofunctional epoxy resin is included as a portion of the epoxy resin component, such resin should be employed in an amount of up to about 20% by weight based on the total epoxy resin component.

The monofunctional epoxy resin should have an epoxy group with an alkyl group of about 6 to about 28 carbon atoms, examples of which include C_6-C_{28} alkyl glycidyl ethers, C_6-C_{28} fatty acid glycidyl esters and C_6-C_{28} alkylphenol glycidyl ethers.

Such epoxy resin(s) include generally, but are not limited to, polyglycidyl ethers of polyvalent phenols, for

example pyrocatechol; resorcinol; hydroquinone; 4,4'-dihydroxydiphenyl methane 4,4'-dihydroxy-3,3'-dimethyldiphenyl methane; 4,4'-dihydroxydiphenyl dimethyl methane; 4,4'-dihydroxydiphenyl methyl methane; 4,4'-dihydroxydiphenyl cyclohexane; 4,4'-dihydroxy-3,3'-dimethyldiphenyl propane; 4,4'dihydroxydiphenyl sulfone; tris(4-hydroxyphyenyl)methane; polyglycidyl ethers of the chlorination and bromination products of the above-mentioned diphenols; polyglycidyl ethers of novolacs (i.e., reaction products of monohydric or polyhydric phenols with aldehydes, formaldehyde in particular, in the presence of acid catalyst; polyglycidyl ethers of diphenols obtained by esterifying 2 moles of the ethers of diphenols obtained by esterifying 2 moles of the sodium salt of an aromatic hydrocarboxylic acid with 1 mole of a dihaloalkane or dihalogen dialkyl ether (see U.K. Pat. No. 1,017,612, the disclosure of which is hereby expressly incorporated herein by reference); and polyglycidyl ethers of polyphenols obtained by condensing phenols and long-chain halogen paraffins containing at least two halogen atoms (see U.K. Pat. No. 1,024,288, the disclosure of which is hereby expressly incorporated herein by reference).

Other suitable epoxy compounds include polyepoxy compounds based on aromatic amines and epichlorohydrin, such as N,N'-diglycidyl-aniline; N,N'-dimethyl-N,N'-diglycidyl-4,4'diaminodiphenyl methane; N,N,N',N'-tetraglycidyl-4,4'diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether; and N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate.

Examples of the multifunctional epoxy resin include bisphenol A-type epoxy resin, bisphenol F-type epoxy resin, phenol novolac-type epoxy resin, and cresol novolac-type epoxy resin.

Among the epoxy resins suitable for use herein are polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradenames EPON 828,

EPON 1001, EPON 1009, and EPON 1031, from Shell Chemical Co.; DER 331, DER 332, DER 334, and DER 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku, Japan. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of which are available commercially under the tradenames DEN 431, DEN 438, and DEN 439 from Dow Chemical Company. Cresol analogs are also available commercially ECN 1235, ECN 1273, and ECN 1299 from Ciba-Geigy Corporation. SU-8 is a bisphenol A-type epoxy novolac available from Interez, Inc. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include GLYAMINE 135, GLYAMINE 125, and GLYAMINE 115 from F.I.C. Corporation; ARALDITE MY-720, ARALDITE 0500, and ARALDITE 0510 from Ciba-Geigy Corporation and PGA-X and PGA-C from the Sherwin-Williams Co.

And of course combinations of the different epoxy resins are also desirable for use herein.

In choosing epoxy resins for the epoxy resin component of the compositions of the present invention, consideration should also be given to viscosity and other properties thereof.

The cyanate esters useful as a component in the latent hardening component may be chosen from aryl compounds having at least one cyanate ester group on each molecule and may be generally represented by the formula $Ar(OCN)_m$, where m is an integer from 2 to 5 and Ar is an aromatic radical. The aromatic radical Ar should contain at least 6 carbon atoms, and may be derived, for example, from aromatic hydrocarbons, such as benzene, biphenyl, naphthalene, anthracene, pyrene or the like. The aromatic radical Ar may also be derived from a polynuclear aromatic hydrocarbon in which at least two aromatic rings are attached to each other through a bridging group. Also included are aromatic radicals derived from novolac-type phenolic resins -- i.e., cyanate esters of these phenolic resins. The aromatic

radical Ar may also contain further ring-attached, non-reactive substituents.

Examples of such cyanate esters include, for instance, 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane; tris(4-cyanatophenyl)-phosphite; tris(4-cyanatophenyl)phosphate; bis(3-chloro-4-cyanatophenyl)methane; cyanated novolac; 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and cyanated bisphenol-terminated polycarbonate or other thermoplastic oligomer.

Other cyanate esters include cyanates disclosed in U.S. Patent Nos. 4,477,629 and 4,528,366, the disclosure of each of which is hereby expressly incorporated herein by reference; the cyanate esters disclosed in U.K. Pat. No. 1,305,702, and the cyanate esters disclosed in International Patent Publication WO 85/02184, the disclosure of each of which is hereby expressly incorporated herein by reference. Of course, combinations of these cyanate esters within the imidizole component of the compositions of the present invention are also desirably employed herein.

A particularly desirable cyanate ester for use herein is available commercially from Ciba Geigy Corporation, Tarrytown, New York under the tradename AROCY 366 (1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene).

The imidizole component of the latent hardener component include imidizoles, such as imidizole and derivatives thereof, such as isoimidizole, imidizole, alkyl substituted imidizoles, such as 2-methyl imidizole, 2-ethyl-4-methylimidizole, 2,4-dimethylimidizole, butylimidizole, 2-heptadecenyl-4-methylimidizole,

2-methylimidizole, 2-undecenylimidizole,
1-vinyl-2-methylimidizole, 2-n-heptadecylimidizole,
2-undecylimidizole, 2-heptadecylimidizole,
2-phenylimidizole, 2-ethyl 4-methylimidizole,
1-benzyl-2-methylimidizole, 1-propyl-2-methylimidizole,
1-cyanoethyl-2-methylimidizole,
1-cyanoethyl-2-ethyl-4-methylimidizole,
1-cyanoethyl-2-undecylimidizole,
1-cyanoethyl-2-phenylimidizole,
1-guanaminoethyl-2-methylimidizole and addition products of an imidizole methylimidizole and addition products of an imidizole and trimellitic acid,
2-n-heptadecyl-4-methylimidizole and the like, generally where each alkyl substituent contains up to about 17 carbon atoms and desirably up to about 6 carbon atoms; aryl substituted imidizoles, such as phenylimidazole, benzylimidizole, 2-methyl-4,5-diphenylimidizole, 2,3,5-triphenylimidizole, 2-styrylimidizole, 1-(dodecyl benzyl)-2-methylimidizole,
2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidizole,
2-(2-methoxyphenyl)-4,5-diphenylimidizole,
2-(3-hydroxyphenyl)-4-,5-diphenylimidizole,
2-(p-dimethylaminophenyl)-4,5-diphenylimidizole,
2-(2-hydroxyphenyl)-4,5-diphenylimidizole,
di(4,5-diphenyl-2-imidizole)-benzene-1,4,
2-napnthyl-4,5-diphenylimidizole,
1-benzyl-2-methylimidizole, 2-p-methoxystyrylimidizole, and the like generally where each aryl substituent contains up to about 10 carbon atoms and desirably up to about 8 carbon atoms.

Of course, combinations of these imidizoles are also desirable as the imidizole component of the latent hardener component of the compositions of the present invention.

The thermosetting resin compositions of the present invention may be of the one-pack type, in which all the ingredients are mixed together, or of the two-pack type in which the epoxy resin component and latent hardener

component are stored separately and mixed together prior to use.

During application, the thermosetting resin compositions according to the present invention penetrate and flow readily into the space between the circuit board and the semiconductor device, or at least show a reduction in viscosity under heated or use conditions thus penetrating and flowing easily.

Generally, it is desirable to prepare the thermosetting resin compositions of this invention by selecting the types and proportions of various so that the gel times will be tailored to a specified period of time (such as 1 minute or 2 minutes) at a temperature of about 150°C. In such case, the inventive compositions should show no or substantially no increase of viscosity after a period of time of about six hours. With such a gel time, the compositions penetrate into the space between the circuit board and the semiconductor device (e.g., of 100 to 200 μm) relatively rapidly, and allow for a greater number of assemblies to be filled without observing a viscosity increase in the composition thereby rendering it less effective for application.

Optionally, the thermosetting resin composition of the present invention may further contain other additives such as defoaming agents, leveling agents, dyes, pigments and fillers. Moreover, the compositions may also contain photopolymerization initiators, provided such materials do not adversely affect the desired properties of the composition.

In an additional aspect of this invention, there is provided filled thermosetting compositions. These compositions, in addition to the epoxy resin component and latent hardener component, include a filler component. The filler component acts to lower moisture pick up, and tends to increase viscosity. Appropriate filler components include silica, alumina, silica-coated aluminum nitride, silver flake and the like.

Generally, about 0.1 to about 300 parts of the

filler component may be used, with about 150 to 180 parts being desirable.

Reference to Figure 1 shows a mounted structure (i.e., a flip chip package) in which a thermosetting resin composition of the present invention has been applied and cured.

The flip chip package 4 is formed by connecting a semiconductor chip (a bare chip) 2 to a carrier substrate 1 (e.g., a circuit board) and sealing the space therebetween suitably with a thermosetting resin composition 3. This semiconductor device is mounted at a predetermined position on the carrier substrate 1, and electrodes 5 and 6 are electrically connected by a suitable electrical connection means 7 and 8, such as solder. In order to improve reliability, the space between the semiconductor chip 2 and the carrier substrate 1 is sealed with a thermosetting resin composition 3, and then cured. The cured product of the thermosetting resin composition should completely fill that space.

Carrier substrates may be constructed from ceramic substrates of Al_2O_3, SiN_3 and mullite (Al_2O_3-SiO_2); substrates or tapes of heat-resistant resins, such as polyimides; glass-reinforced epoxy; ABS and phenolic substrates which are also used commonly as circuit boards; and the like. Any electrical connection of the semiconductor chip to the carrier substrate may be used, such as connection by a high-melting solder or electrically (or anisotropically) conductive adhesive, wire bonding, and the like. In order to facilitate connections, the electrodes may be formed as bumps.

In a typical mounting process, solder ball (e.g., in cream or form) may be printed at appropriate positions on a carrier substrate and suitably dried to expel solvent. A semiconductor chip may then mounted in conformity with the pattern on the carrier substrate. This carrier substrate is then passed through a reflowing furnace to melt the solder to connect the semiconductor chip. Moreover, the solder may be applied or formed on either the carrier substrate or the

semiconductor chip. Alternatively, this connection may also be made by an electrically conductive adhesive or an anisotropically conductive adhesive.

After the semiconductor chip is electrically connected to the carrier substrate, the resulting structure is ordinarily subjected to a continuity test or the like. After passing such test, the semiconductor chip may be fixed thereto with a thermosetting resin composition, as described below. In this way, in the event of a failure, the semiconductor chip may be removed before it is fixed to the carrier substrate with the thermosetting resin composition.

Using a suitable application means, such as a dispenser, a thermosetting resin composition in accordance with this invention is applied to the periphery of the electronically-connected semiconductor chip. The composition penetrates by capillary action into the space between the carrier substrate and the semiconductor chip.

The thermosetting resin composition is then thermally cured by the application of heat. During the early stage of this heating, the thermosetting resin composition shows a significant reduction in viscosity and hence an increase in fluidity, so that it more easily penetrates into the space between the carrier substrate and the semiconductor chip. Moreover, by preheating the carrier substrate, the thermosetting resin composition is allowed to penetrate fully into the entire space between the carrier substrate and the semiconductor chip.

Cured reaction products of the thermosetting resin compositions of the present invention demonstrate excellent adhesive force, heat resistance and electric properties, and acceptable mechanical properties, such as flex-cracking resistance, chemical resistance, moisture resistance and the like, for the applications for which they are used herein.

The amount of thermosetting resin composition applied should be suitably adjusted so as to fill almost completely the space between the carrier substrate and the semiconductor chip, which amount of course may vary depending on application.

Thermosetting resin compositions of the present invention may ordinarily be cured by heating to a temperature in the range of about 120 to about 180°C for a period of time of about 0.5 to 30 minutes. However, generally after application of the composition, an initial cure time of about 1 minute sets up the composition, and complete cure is observed after about 15 minutes at 150°C. Thus, the composition of the present invention can be used in relatively moderate temperatures and short-time curing conditions, and hence achieve very good productivity.

The present invention will be more readily appreciated with reference to the examples which follow.

EXAMPLES

In these examples, compositions in accordance with the present invention were prepared and evaluated for performance in contrast with compositions prepared without the cyanate ester component of the latent hardener component. Results are set forth below.

Example 1

Thermosetting Resin Composition -- 1 Minute Gel Time

A. A thermosetting resin composition for underfill applications in accordance with the present invention was prepared by mixing together with stirring for a period of time of about 10 minutes at room temperature in an open vessel an epoxy resin component including 92 parts by weight of bisphenol F-type epoxy resin, and a latent hardener component including 4 parts by weight of 2-ethyl-4-methylimidizole, and 4 parts by weight of 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene as a cyanate ester resin (commercially available under the tradename AROCY 366 from Ciba-Geigy).

While the composition was used upon formation, it may be stored for a period of time of up to about 3 to about 6 months at a temperature of about -20°C without experiencing viscosity increase.

After formation, the composition was transferred

to a 10 ml syringe made of non-reactive plastic, and the composition was dispensed through the 12G needle of the syringe into the junction between the carrier substrate and semiconductor chip in a previously-formed assembly. As such, the composition acts as an encapulant for the electrical solder connection.

After dispensing was complete, the assembly was transferred to an oven while the temperature was maintained at about 150°C. The composition cured initially after about 1 minute, and thereafter cured completely after about 15 minutes at that temperature.

Separately, the composition was placed between a pair of lap shears and cured in the same way as the assembly above. The bound lap shears were removed from the oven and allowed to reach room temperature, at which point they were evaluated for bond strength. The cured composition was found to possess lap shear strength of about 1660 psi -- which is acceptable for the microelectronic applications which the compositions are designed.

With respect to shelf-life stability, as noted above the gel time of the composition was tailored to 1 minute at a temperature of 150°C. This composition was observed to experience no viscosity increase at room temperature after a period of time of 6 hours; after a period of time of about 15 hours the viscosity increase was observed to be about 52%; and after a period of time of about 24 hours the viscosity increase was observed to be about 88%.

B. A comparable composition was prepared in which no cyanate ester was added. That composition included 96.5 parts bisphenol F-type epoxy resin and 3.5 parts of 2-ethyl-4-methylimidizole. The composition was also tailored to a gel time of about 1 minute at a temperature of 150°C. The lap shear strength was observed to be about 1670 psi.

This composition was applied as above, and demonstrated a viscosity increase at room temperature after a period of time of about 6 hours of about 13%; after a

period time of about 15 hours of about 153% and after a period of time of 24 hours of about 267%.

Accordingly, it is seen that the presence of the cyanate ester component in the inventive compositions has a dramatic affect in maintaining a useful working life for the compositions with respect to slowing viscosity increase over time at room temperature.

Example 2

Thermosetting Resin Composition -- 2 Minute Gel Time

A. A thermosetting resin composition for underfill applications in accordance with the present invention was prepared by mixing together with stirring for a period of time of about 10 minutes at room temperature in an open vessel an epoxy resin component including 88 parts by weight of bisphenol F-type epoxy resin, and a latent hardener component including 8 parts by weight of 2-ethyl-4-methylimidizole, and 4 parts by weight of 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene as a cyanate ester resin (AROCY 366).

While this composition was used upon formation, it too may be stored for a period of time of up to about 3 to about 6 months at a temperature of about -20°C without experiencing viscosity increase.

After formation, the composition was transferred to a 10ml syringe made of non-reactive plastic, and the composition was dispensed through the 12G needle of the syringe into the junction between the carrier substrate and semiconductor chip in a previously-formed assembly to act as an encapulant for the electrical solder connection.

After dispensing was complete, the assembly was transferred to an oven while the temperature was again maintained at about 150°C. The composition cured initially after about 2 minutes, and thereafter cured completely after about 15 minutes at that temperature.

This composition was also placed between a pair of lap shears and cured in the same way as the assembly above, and as in Example 1. The lap shears were removed from the

oven and allowed to reach room temperature, at which point they were evaluated for bond strength. The cured composition was found to possess lap shear strength of about 1620 psi -- which is acceptable for the microelectronic applications for which the compositions are designed.

With respect to shelf-life stability, as noted above the gel time of the composition was tailored to 2 minute at a temperature of 150°C. This composition was observed to experience a viscosity increase at room temperature after a period of time of 6 hours of about 3%; after a period of time of about 15 hours the viscosity increase was observed to be about 10%; and after a period of time of about 24 hours the viscosity increase was observed to be about 20%.

B. A comparable composition was prepared in which no cyanate ester was added. That composition included 97.5 parts bisphenol F-type epoxy resin and 2.5 parts of 2-ethyl-4-methylimidizole. The composition was also tailored to a gel time of about 2 minutes at a temperature of 150°C. The lap shear strength was observed to be about 1600 psi.

This composition was applied as above, and demonstrated a viscosity increase at room temperature after a period of time of about 6 hours of about 16%; after a period time of about 15 hours of about 82% and after a period of time of 24 hours of about 162%.

Accordingly, it is seen that the presence of the cyanate ester in the inventive compositions has a dramatic affect in maintaining a useful working life for the compositions with respect to slowing viscosity increase over time at room temperature.

What Is Claimed Is:

1. A thermosetting resin composition capable of sealing underfilling between a semiconductor device and a circuit board to which said semiconductor device is electrically connected, said composition comprising:

(a) an epoxy resin component; and

(b) a latent hardener component comprising

(i) a cyanate ester component; and

(ii) an imidizole component.

2. The composition of Claim 1, wherein said epoxy resin comprises at least one multifunctional epoxy resin.

3. The composition according to Claim 1, wherein the epoxy resin component includes members selected from the group consisting of C_6-C_{28} alkyl glycidyl ethers; C_6-C_{28} fatty acid glycidyl esters; C_6-C_{28} alkylphenol glycidyl ethers; polyglycidyl ethers of pyrocatechol, resorcinol, hydroquinone, 4,4'-dihydroxydiphenyl methane, 4,4'-dihydroxy-3,3'-dimethyldiphenyl methane, 4,4'-dihydroxydiphenyl dimethyl methane, 4,4'-dihydroxydiphenyl methyl methane, 4,4'-dihydroxydiphenyl cyclohexane, 4,4'-dihydroxy-3,3'-dimethyldiphenyl propane, 4,4'dihydroxydiphenyl sulfone, and tris(4-hydroxyphyenyl)methane; polyglycidyl ethers of the chlorination and bromination products of the above-mentioned diphenols; polyglycidyl ethers of novolacs; polyglycidyl ethers of diphenols obtained by esterifying ethers of diphenols obtained by esterifying salts of an aromatic hydrocarboxylic acid with a dihaloalkane or dihalogen dialkyl ether; polyglycidyl ethers of polyphenols obtained by condensing phenols and long-chain halogen paraffins containing at least two halogen atoms; N,N'-diglycidyl-aniline; N,N'-dimethyl-N,N'-diglycidyl-4,4'diaminodiphenyl methane;

N,N,N',N'-tetraglycidyl-4,4'diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether; N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate; bisphenol A epoxy resin, bisphenol F epoxy resin, phenol novolac epoxy resin, and cresol novolac epoxy resin.

4. The composition according to Claim 1, wherein the epoxy resin component includes bisphenol F epoxy resin and epoxy cresol novalac resin.

5. The composition according to Claim 1, wherein the epoxy resin component includes about 80 parts bisphenol F epoxy resin and about 20 parts epoxy cresol novalac resin.

6. The composition according to Claim 1, wherein the latent hardener component is employed in an amount within the range of from 0 to about 30 parts.

7. The composition according to Claim 1, wherein the cyanate ester component is chosen from aryl compounds having at least one cyanate ester group on each molecule.

8. The composition according to Claim 1, wherein the cyanate ester component is represented by $Ar(OCN)_m$, wherein Ar is an aromatic radical and m is an integer from 2 to 5.

9. The composition according to Claim 1, wherein the cyanate ester component is selected from the group consisting of 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane;

tris(4-cyanatophenyl)-phosphite;
tris(4-cyanatophenyl)phosphate;
bis(3-chloro-4-cyanatophenyl)methane; cyanated novolac;
1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and
cyanated bisphenol-terminated polycarbonate or other
thermoplastic oligomer.

10. The composition according to Claim 1, wherein the cyanate ester component is 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene.

11. The composition according to Claim 1, wherein the cyanate ester component is employed in an amount within the range of 0 to about 15 parts.

12. The composition according to Claim 1, wherein the imidizole component is a member selected from the group consisting of imidizole, isoimidizole, 2-methyl imidizole, 2-ethyl-4-methylimidizole, 2,4-dimethylimidizole, butylimidizole, 2-heptadecenyl-4-methylimidizole, 2-methylimidizole, 2-undecenylimidizole, 1-vinyl-2-methylimidizole, 2-n-heptadecylimidizole, 2-undecylimidizole, 2-heptadecylimidizole, 2-phenylimidizole, 1-benzyl-2-methylimidizole, 1-propyl-2-methylimidizole, 1-cyanoethyl-2-methylimidizole, 1-cyanoethyl-2-ethyl-4-methylimidizole, 1-cyanoethyl-2-undecylimidizole, 1-cyanoethyl-2-phenylimidizole, 1-guanaminoethyl-2-methylimidizole and addition products of an imidizole methylimidizole and addition products of an imidizole and trimellitic acid, 2-n-heptadecyl-4-methylimidizole, phenylimidazol, benzylimidizole, 2-methyl-4,5-diphenylimidizole, 2,3,5-triphenylimidizole, 2-styrylimidizole, 1-(dodecyl benzyl)-2-methylimidizole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidizole, 2-(2-methoxyphenyl)-4,5-diphenylimidizole, 2-(3-hydroxyphenyl)-4-,5-diphenylimidizole,

2-(p-dimethyl-aminophenyl)-4,5-diphenylimidizole,
2-(2-hydroxyphenyl)-4,5-diphenylimidizole,
di(4,5-diphenyl-2-imidizole)-benzene-1,4,
2-napnthyl-4,5-diphenylimidizole,
1-benzyl-2-methylimidizole, 2-p-methoxystyrylimidizole, and the combinations thereof.

13. The composition according to Claim 1, wherein the imidizole component is 2-ethyl-4-methylimidizole.

13. The composition according to Claim 1, wherein the imidizole component is employed in an amount within the range of 0 to about 15 parts.

14. A thermosetting resin composition capable of sealing underfilling between a semiconductor device and a circuit board to which said semiconductor device is electrically connected, said composition comprising:

(a) about 92 parts by weight of an epoxy resin component comprising bisphenol F epoxy resin, and

(b) about 8 parts by weight of latent hardening component, of which 4 parts is comprised of (i) a cyanate ester component comprising 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and 4 parts is comprised of (ii) an imidizole component comprising 2-ethyl-4-methylimidizole.

15. A thermosetting resin composition capable of sealing underfilling between a semiconductor device and a circuit board to which said semiconductor device is electrically connected, said composition comprising:

(a) about 88 parts by weight of an epoxy resin component comprising bisphenol F epoxy resin, and

(b) about 12 parts by weight of latent hardening component, of which 4 parts is comprised of a cyanate ester component comprising 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and 8 parts is comprised of an imidizole component comprising

2-ethyl-4-methylimidizole.

16. The composition of Claim 1, having a viscosity of less than about 50,000 mPa·s at a temperature of 25°C.

17. Reaction products according to any one of Claims 1-16.

18. A mounting structure for semiconductor devices, comprising:

a semiconductor device comprising a semiconductor chip mounted on a carrier substrate, and

a circuit board to which said semiconductor device is electrically connected,

wherein the space between the carrier substrate of said semiconductor device and said circuit board is sealed with a reaction product of a thermosetting resin composition comprising an epoxy resin component, and a latent hardener component comprising a cyanate ester component, and an imidizole component.

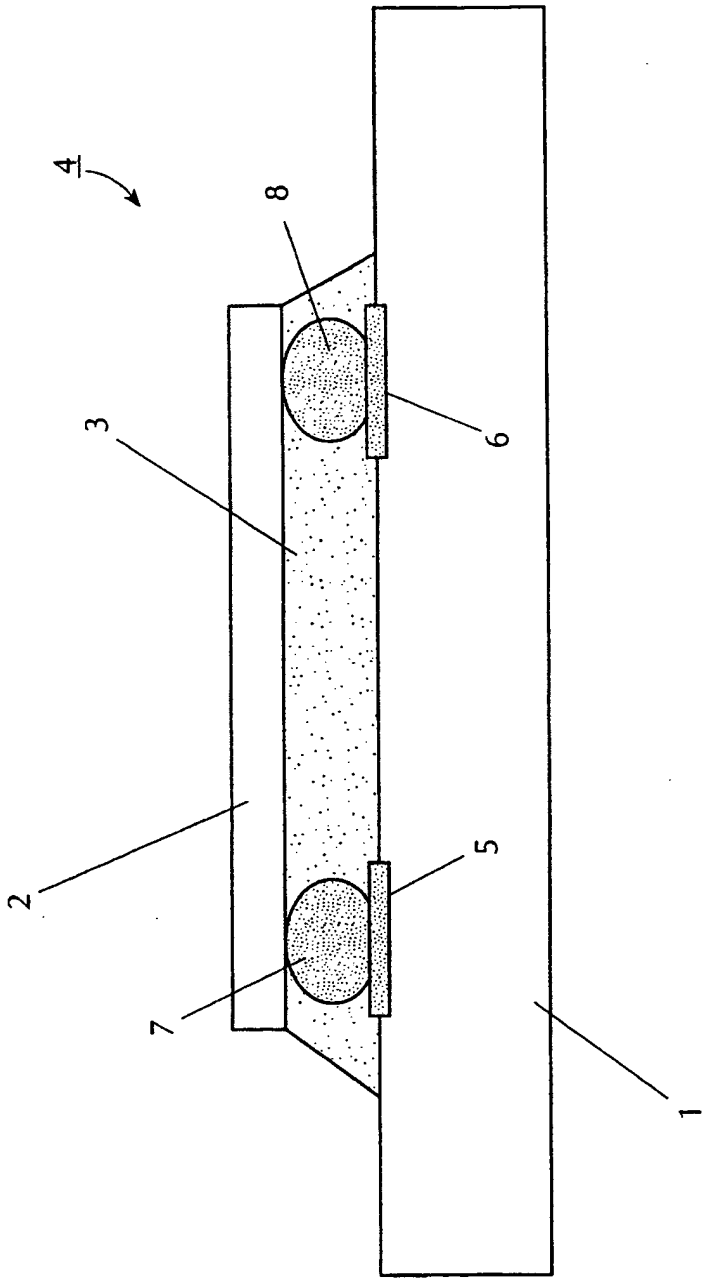
19. The mounting structure according to Claim 18, wherein the thermosetting resin composition is in accordance with Claims 14 or 15.

20. A process for fabricating semiconductor devices, said process comprising the steps of:

electrically connecting a semiconductor device comprising a semiconductor chip mounted on a carrier substrate, to a circuit board;

infiltrating a thermosetting resin composition into the space between the carrier substrate of said semiconductor device and said circuit board, wherein the composition comprises an epoxy resin component; and a latent hardener component comprising a cyanate ester component, and an imidizole component; and curing the composition by the application of heat.

FIG. 1



INTERNATIONAL SEARCH REPORT

national application No.
PCT/US98/15578

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08G 59/68; H01L 23/02
US CL :528/93, 94; 174/52.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/93, 94; 174/52.5

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,330,684 A (EMORI et al.) 19 July 1994, see entire document.	1-20
Y	US 5,534,356 A (MAHULIKAR et al.) 09 July 1996, see entire document.	18-20
Y	US 4,159,976 A (MORAN, JR.) 03 July 1979, see entire document.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
04 OCTOBER 1998	29 OCT 1998
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARGARET GLASS Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

The demand must be filed directly with the competent International Examining Authority or, if two or more Authorities are competent, with the one chosen by the applicant. The full name or two-letter code of that Authority may be indicated by the applicant on the line below:
IPEA/ US

PCT

CHAPTER II

DEMAND

Under Article 31 of the Patent Cooperation Treaty:
The undersigned requests that the international application specified below be the subject of International preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).

For International Preliminary Examining Authority use only

Identification of IPEA	Date of receipt of DEMAND

Box No. I IDENTIFICATION OF THE INTERNATIONAL APPLICATION

Applicant's or agent's file reference: **ICC-196 PCT**

International application No.	International filing date *(day/month/year)*	(Earliest) Priority date *(day/month/year)*
PCT/US00/11878	**16 JUNE 2000 (16.06.00)**	**17 JUNE 1999 (17.06.99)**

Title of invention: **REWORKABLE THERMOSETTING RESIN COMPOSITIONS**

Box No. II APPLICANT(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

LOCTITE CORPORATION
1001 Trout Brook Crossing
Rocky Hill, Connecticut 06067
US

Telephone No.: **860.571.5000**
Facsimile No.: **860.571.5465**
Teleprinter No.:

State *(that is, country)* of nationality: **US**
State *(that is, country)* of residence: **US**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

DOBA, Takahisa
3-18-7 Noukendai
Kanazawa-Ku
JAPAN

State *(that is, country)* of nationality: **JP**
State *(that is, country)* of residence: **JP**

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

State *(that is, country)* of nationality:
State *(that is, country)* of residence:

☐ Further applicants are indicated on a continuation sheet.

Form PCT/IPEA/401 (first sheet) (July 1998; reprint July 1999) *See Notes to the demand form*

International application No.
PCT/US00/11878

Box No. III AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The following person is [X] Agent [ ] common representative

and [X] has been appointed earlier and represents the applicant(s) also for international preliminary examination.

[ ] is hereby appointed and any earlier appointment of (an) agent(s)/common representative is hereby revoked.

[ ] is hereby appointed, specifically for the procedure before the International Preliminary Examining Authority, in addition to the agent(s)/common representative appointed earlier.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

BAUMAN, Steven C.
LOCTITE CORPORATION
1001 Trout Brook Crossing
Rocky Hill, Connecticut 06067
US

Telephone No.: 860.571-5001
Facsimile No.: 860.571.5028
Teleprinter No.:

[ ] **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Box No. IIV BASIS FOR INTERNATIONAL PRELIMINARY EXAMINATION

Statement concerning amendments:*

1. The applicant wishes the international preliminary examination **to start on the basis of:**

[X] the international application as originally filed

the description
- [ ] as originally filed
- [X] as amended under Article 34

the claims
- [ ] as originally filed
- [ ] as amended under Article 19 (together with any accompanying statement)
- [ ] as amended under Article 34

the drawings
- [ ] as originally filed
- [X] as amended under Article 34

2. [ ] The applicant wishes any amendment to the claims under Article 19 to be considered reversed.

3. [ ] The applicant wishes the start of the international preliminary examination **to be postponed** until the expiration of 20 months from the priority date unless the International Preliminary Examining Authority receives a copy of any amendments made under Article 19 or a notice from the applicant that he does not wish to make such amendments (Rule 69.1(d)). *(This check-box may be marked only where the time limit under Article 19 has not yet expired.)*

* Where no check-box is marked, international preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.

Language for the purposes of international preliminary examination: ..... **English** .....

- [X] which is the language in which the international application was filed.
- [ ] which is the language of a translation furnished for the purposes of international search.
- [ ] which is the language of publication of the international application.
- [ ] which is the language of the translation (to be) furnished for the purposes of international preliminary examination.

Box No. V ELECTION OF STATES

The applicant hereby **elects all eligible States** *(that is, all States which have been designated and which are bound by Chapter II of the PCT)*

excluding the following States which the applicant wishes **not to elect:**

International application No.
PCT/US00/11878

Box No. VI CHECK LIST

The demand is accompanied by the following elements, in the language referred to in Box No. IV, for the purposes of international preliminary examination:

					For International Preliminary Examining Authority use only: received	not received
1.	translation of international application	:		sheets	☐	☐
2.	amendments under Article 34	:	9	sheets	☐	☐
3.	copy (or, where required, translation) of amendments under Article 19	:		sheets	☐	☐
4.	copy (or, where required, translation) of statement under Article 19	:		sheets	☐	☐
5.	letter	:		sheets	☐	☐
6.	other *(specify)*	:		sheets	☐	☐

The demand is also accompanied by the item(s) marked below:

1. [X] fee calculation sheet
2. [ ] separate signed power of attorney
3. [ ] copy of general power of attorney; reference number, if any:
4. [ ] statement explaining lack of signature
5. [ ] nucleotide and or amino acid sequence listing in computer readable form
6. [X] other *(specify)*: RETURN RECEIPT POSTCARD

Box No. VII SIGNATURE OF APPLICANT, AGENT OR COMMON REPRESENTATIVE

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the demand).

BAUMAN, Steven C., Agent
(Registration No. 33,832)

For International Preliminary Examining Authority use only

1. Date of actual receipt of DEMAND:
2. Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b):
3. [ ] The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and item 4 or 5, below, does not apply. [ ] The applicant has been informed accordingly.
4. [ ] The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.
5. [ ] Although the date of receipt of the demand is after the expiration of 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.

For International Bureau use only

Demand received from IPEA on:

PCT

CHAPTER II

FEE CALCULATION SHEET

Annex t the Demand for international preliminary examinati n

International application No.	**PCT/US00/11878**
Applicant's or agent's file reference	**ICC-196 PCT**

For International Preliminary Examining Authority use only

Date stamp of the IPEA

Applicant

LOCTITE CORPORATION
DOBA, Takahisa

Calculation of prescribed fees

1.	Preliminary examination fee	**490.00**	**P**
2.	Handling fee *(Applicants from certain States are entitled to a reduction of 75% of the handling fee. Where the applicant is (or all applicants are) so entitled, the amount to be entered at H is 25% of the handling fee.)*	**153.00**	**H**
3.	Total of prescribed fees Add the amounts entered at P and H and enter total in the TOTAL box	**643.00**	**TOTAL**

Mode of Payment

[X]	authorization to charge deposit account with the IPEA (see below)	[ ]	Cash
[ ]	Cheque	[ ]	Revenue stamps
[ ]	postal money order	[ ]	Coupons
[ ]	bank draft	[ ]	Other *(specify)*:

Deposit Account Authorization *(this mode of payment may not be available at all IPEAs)*

The IPEA/ US [X] is hereby authorized to charge the total fees indicated above to my deposit account.

[X] *(this check-box may be marked only if the conditions for deposit accounts of the IPEA so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

12-2135	8 December 2000	Steven C. Bauman
Deposit Account Number	Date *(day/month/year)*	Signature

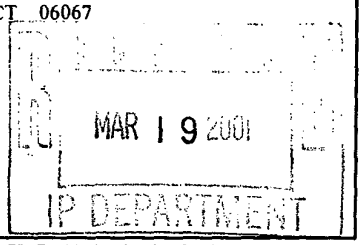
Form PCT/IPEA/401 (Annex) (January 1996; reprint January 1998)

See Notes to the fee calculation sheet

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: STEVEN C. BAUMAN
LOCTITE CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067



PCT

WRITTEN OPINION

(PCT Rule 66)

RJP 3/19/01

Date of Mailing *(day/month/year)*	14 MAR 2001
Applicant's or agent's file reference: ICC-196 PCT	**REPLY DUE** within **TWO** months from the above date of mailing: 14 MAY 01

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US00/11878	16 JUNE 2000	17 JUNE 1999

International Patent Classification (IPC) or both national classification and IPC
Please See Supplemental Sheet.

Applicant
LOCTITE CORPORATION

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I [X] Basis of the opinion
- II [ ] Priority
- III [ ] Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV [ ] Lack of unity of invention
- V [X] Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI [ ] Certain documents cited
- VII [ ] Certain defects in the international application
- VIII [X] Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension., see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 17 OCTOBER 2001.

Name and mailing address of the IPEA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ROBERT SELLERS
Facsimile No. (703) 305-3230	Telephone No. (703) 308-2399

Form PCT/IPEA/408 (cover sheet) (July 1998)★

WRITTEN OPINION

International application No.
PCT/US00/11878

I. Basis of the opinion

1. With regard to the elements of the international application:*

[ ] the international application as originally filed

[X] the description:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

[X] the claims:
pages (See Attached), as originally filed
pages _____, as amended (together with any statement) under Article 19
pages _____, filed with the demand
pages _____, filed with the letter of _____

[X] the drawings:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

[X] the sequence listing part of the description:
pages (See Attached), as originally filed
pages _____, filed with the demand
pages _____, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

[ ] contained in the international application in printed form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. [X] The amendments have resulted in the cancellation of:

[X] the description, pages NONE

[X] the claims, Nos. NONE

[X] the drawings, sheets/~~fig~~ NONE

5. [ ] This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*

WRITTEN OPINION

International application No.
PCT/US00/11878

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	31-49NONE	YES
	Claims	1-30	NO
Inventive Step (IS)	Claims	31-49	YES
	Claims	1-30	NO
Industrial Applicability (IA)	Claims	1-49	YES
	Claims	NONE	NO

2. citations and explanations

Claims 1-3, 9, 11-30 lack novelty under PCT Article 33(2) as being anticipated by U.S. Patent No. 5,512,613 (AFZALI-ARDAKANI et al.).

AFZALI-ARDAKANI et al. (columns 9-10, Example 7 and column 14, Example 23) shows a cleavable composition for providing an underfill between a semiconductor chip and a substrate (column 7, lines 9-14 and 22-24) comprising a ketal diepoxide, hexahydrophthalic anhydride and an imidazole.

Claims 1, 8, 11, 12 and 25-28 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 11-17074 (CHIBA et al.).

CHIBA et al. shows an underfill situated between a semiconductor device and a substrate comprising xylene bis-oxetane (Chemical abstracts registry no. 142627-97-2 according to page 11, lines 16-17 of the description) and a sulfonium salt curing catalyst.

Claims 1, 2 and 10-12 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 8-12741 (NEW JAPAN CHEM CO LTD).

NEW JAPAN CHEM CO LTD discloses a formulation of 1,4-cyclohexane dimethanol diglycidyl ether and an anhydride curing agent.

Claims 1, 8, 11 and 12 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 9-316421 (YAMAMOTO et al.).

YAMAMOTO et al. sets forth an adhesive prepared from bis[4-(2,3-epoxypropylthio)phenyl]sulfide and Sanaid SI 60 L (an aromatic sulfonium salt curing catalyst).

(Continued on Supplemental Sheet.)

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claims 19-22 are objected to under PCT Rule 66.2(a)(v) as lacking clarity under PCT Article 6 because there is no antecedent basis in claim 13 from which claims 19-22 depend for the modified amine compounds of claims 19-21 and the modified imidazole compounds of claim 22. Claim 13 does not define any modified forms of amine compounds or imidazole compounds.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII Sheet 10

TIME LIMIT:

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:
IPC(7): H01L 21/56, 21/58; C08K 03/36; C08L 63/00, 69/00, 71/00 and US Cl.: 428/901; 438/127; 523/466; 524/609, 612; 525/480, 486, 504, 523, 526, 533

I. BASIS OF OPINION:

This opinion has been drawn on the basis of the description:
page(s) 1-17,19-24,26-28, 31-40, as originally filed.
page(s) 18, 25, 29-30, filed with the demand.
and additional amendments:
NONE

This opinion has been drawn on the basis of the claims:
page(s) 41-49, as originally filed.
page(s) NONE, as amended under Article 19.
page(s) NONE, filed with the demand.
and additional amendments:
NONE

This opinion has been drawn on the basis of the drawings:
page(s) 2,4-9, as originally filed.
page(s) 1,3, filed with the demand.
and additional amendments:
NONE

This opinion has been drawn on the basis of the sequence listing part of the description:
page(s) NONE, as originally filed.
pages(s) NONE, filed with the demand.
and additional amendments:
NONE

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
Claims 1, 8 and 11-22 lack novelty under PCT Article 33(2) as being anticipated by the Vysokomol. Soedin., Ser. A article by SERGEEV et al. entitled "Diglycidyl aromatic thio ethers and epoxy polymers derived from them."

SERGEEV et al. describes a composition containing bis[4-(2,3-epoxypropylthio)phenyl]sulfide and an aromatic S-containing diamine curing agent.

Claims 1, 4-6 and 9-22 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 58-42290 (HITACHI CHEMICAL CO., LTD.), Japanese Patent No. 5-271389 (YONEZAWA et al.) or Japanese Patent No. 2-18412 (OISHI et al.).

HITACHI CHEMICAL CO., LTD., YONEZAWA et al. or OISHI et al. espouse compositions obtained from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 29-31 of the description) and a heterocyclic polyamine, ketimine or polyamideamine curing agent, respectively.

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII Sheet 11

Claims 1, 2, 4-6 and 9-22 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 63-159426 (SUMITOMO BAKELITE CO., LTD.)

SUMITOMO BAKELITE CO., LTD. is directed to a blend of a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 20-21 of the description), a bisphenol A epoxy resin, an anhydride curing agent and 2-ethyl-4-methylimidazole as an accelerator.

Claims 1, 3-6, 9-22 and 24 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 62-295029 (MATSUYAMA).

MATSUYAMA shows a sealant derived from a propoxylated bisphenol A diglycidyl ether (i.e. BPO-20E corroborated by Chemical abstracts registry no. 11121-15-6 and deemed to be suitable on page 15, lines 20-21 of the description), a novolak epoxy resin, a novolak phenolic resin hardener, an imidazole accelerator and an aluminum oxide filler.

Claims 1, 2 and 9-22 lack novelty under PCT Article 33(2) as being anticipated by Japanese Patent No. 6-136092 (YAMANAKA et al.)

YAMANAKA et al. is drawn to a sealant comprising 1,4-cyclohexane dimethanol diglycidyl ether, a hydrogenated bisphenol A diglycidyl ether and an anhydride curing agent.

Claims 1, 7, 8, 11 and 12 lack novelty under PCT Article 33(2) as being anticipated by the J. Macromol. Sci., Pure Appl. Chem. article by CRIVELLO et al. entitled "Structure and reactivity relationships in the photoinitiated cationic polymerization of oxetane monomers."

CRIVELLO et al. discloses a carbonate bis-oxetane (Chemical abstracts registry no. 60763-95-3P according to page 12, lines 19-20 of the description) cured with a phenyliodonium or phenylsulfonium fluoroantimonate.

Each of the references applied hereinabove employ species of epoxy resins within the purview of the claimed structures or chemical names. Although the claimed "reaction products of which are controllably degradable" in claim 1, lines 1-2 are not explicitly recited, the structures of the epoxy resins of the cited prior art inherently exhibit controllable degradability based on the identical structures of the epoxy resins of the prior art and claims.

Claims 1-30 meet the criteria set out in PCT Article 33(4) due to the industrial applicability of the composition as an underfill sealant for a semiconductor chip mounted on a substrate.

---------- NEW CITATIONS ----------

JP 10-1657 A2 (SHINKO CHEMICAL CO., LTD.) 06 January 1998, abstract identifying Sanaid SI 60L of JP 9-3164221 A2 as an aromatic sulfonium salt.

CRIVELLO et al. Structure and reactivity relationships in the photoinitiated cationic polymerization of oxetane monomers. J. Macromol. Sci., Pure Appl. Chem. 1993, Vol. A30, No. 2-3, pages 189-206, Chemical abstract accession no. 1993:7419 and Chemical abstract registry no. 60763-95-3P.